THE DEVELOPMENT OF

A RAPID CHLORIDE TEST FOR CONCRETE

AND ITS USE IN ENGINEERING PRACTICE

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Prepared for: The Faculty of Engineering at the University of Cape Town.

JULY 1997

Thesis prepared in fulfilment of the requirements for the degree of PhD.

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ACKNOWLEDGEMENTS

I am indebted to many people and organizations who contributed to this project and were essential to the overall success of the work. My appreciation is extended to the following:

- my supervisor Professor Mark Alexander for his assistance throughout this research;
- Technikon students who assisted in the laboratory, Andrew Swanepoel, Marc du Plessis, Jeffrey Daniels, Elliot Johnson and Bruce Manuel;
- The S.A. cement industry and in particular Anglo Alpha, Pretoria Portland Cement and the Foundation for Research Development for their financial support;
- workshop and laboratory staff.

Finally I thank my wife and parents for their support during this period.

ABSTRACT

This thesis is concerned with rapid chloride testing of concrete. In particular, it describes the development of the rapid chloride conductivity test which measures the physical resistance of concrete to the transport of chloride ions. The test was developed to be used in engineering practice for, inter alia:-

- marine concrete durability research
- predicting long-term chloride ingress into concrete
- construction quality control.

The test is of low cost, has a sound theoretical basis, and as far as can be ascertained, is the most rapid of all chloride tests developed to date. Due to the short test duration, it is possible to test concretes cured for very short periods. Samples can also be left immersed in chloride solution and re-tested at later ages to study time-dependent phenomena such as chloride binding.

The chloride conductivity test involves the standardisation of the concrete pore solution by vacuum-saturating a concrete sample with a 5 M NaCl solution. A single conductivity measurement of the sample is then performed. Different concrete samples yield different conductivities primarily because of differences in their pore and micro-structure. The measured conductivity is related to the diffusibility ratio as well as to the theoretical steady state chloride diffusivity of concrete. Trial tests were performed to determine the optimum conditions for the test (sample conditioning, test procedure) and to verify the test relationships.

The conductivity test apparatus was designed to:

- accurately measure DC conductivity
- be inexpensive and easy to use
- allow rapid changeover from one sample to another.

The chloride conductivity test was standardised by means of a ruggedness test (ASTM E 1169-89), which determines the allowable ranges in the critical variables involved in the test method. Proper control over these variables was subsequently set out in the test method specifications. The single-operator coefficient of variation of the test is estimated to be 6 %.

while the range of typical test results may span approximately two orders of magnitude. The test is therefore very sensitive to the measured property.

An extensive laboratory- and site-based experimental programme was carried out to demonstrate the possibility of using the test for the purposes stated. The laboratory tests involved the durability characterisation of a range of concrete mixes using the chloride conductivity test, an oxygen permeability test and a water sorptivity test. The site tests involved correlating the test results with chloride ingress in-situ in a marine environment.

The chloride conductivity test was shown to be suitable for durability research due to the following characteristics:

- high precision
- sound theoretical basis
- short test duration.

The good correlation obtained between the chloride conductivity results and in-situ chloride ingress parameters verified the potential of the test to predict chloride ingress. The test should ideally be coupled with a chloride ingress model if it is to be used for the prediction of long-term chloride ingress. Such a chloride ingress model based on the chloride conductivity test has recently been developed in the UCT laboratory.

The chloride conductivity test can be used for construction quality control as it is sensitive to most of the quality-related parameters:

- water/cement ratio
- cement type
- cement content
- curing
- compaction

For quality control purposes the test can be thought of as an index or characterisation test, since it yields a reproducible measure of the physical resistance of concrete to the passage of chloride ions. The use of such a durability index test in conjunction with a covermeter survey after construction would help ensure compliance with specifications.

The work done has indicated the possibility of developing a further test that would give a

rapid indication of the chloride binding characteristics (chemical resistance to chloride ingress) of concrete. The test would involve saturating concrete with a lower concentration chloride solution (1 - 3 M NaCl) and then measuring the reduction in conductivity with time. With lower concentration chloride solutions, the test becomes very sensitive to a reduction in chloride concentration in the pore solution due to chloride binding.

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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND TO STUDY

Reinforcement corrosion resulting from chloride ingress is the greatest durability problem of reinforced concrete structures in marine environments. Marine concrete structures exhibiting rust stains, cracking and spalling are a common sight. Repair of this damage requires the removal of all areas of chloride-contaminated concrete, or permanent cathodic protection. These processes are difficult and expensive. Adequate durability design at the outset is therefore increasingly being seen as imperative.

Existing durability specifications (which prescribe mix parameters, materials, cover depths, curing and compaction) for marine concrete were found to be inadequate by Mackechnie (1996) due to the dependence of durability properties on cement composition and the difficulty in testing for compliance on site. A more rational approach using performance-based specifications was proposed: this would involve specifying a measurable early-age property which relates to the long-term performance of concrete.

Concrete is a porous material, and deleterious substances enter concrete through the pore space. The rate at which these substances move through the concrete pore space largely determines the rate at which degradation proceeds. For concrete exposed to marine tidal or submerged zones, chlorides enter mainly via the transport mechanism of diffusion. Corrosion is then possible after a certain threshold chloride level at the steel is exceeded.

A test that measures the diffusivity of concrete therefore seems appropriate. However, diffusion is a very slow process, and laboratory diffusion tests are generally of too long duration to be of practical use for routine testing. Rapid chloride tests have been developed which utilise an electric potential difference to accelerate the transport of chloride ions through the concrete. These tests can have serious problems associated with them such as:

- The interference of mobile ions present in the concrete on the test results.
- Non-standardised and poor control over the critical variables in the test method.
- Too long duration.
- The absence of confident and significant correlations with the performance of concrete in-situ.

The need for a new rapid chloride test which estimates the chloride diffusivity of concrete accurately in the absence of outside influences was therefore identified.

1.2 OBJECTIVES OF THESIS

The objective of this thesis was the development of a chloride test which:

- estimates the steady state diffusivity of concrete accurately and has a sound theoretical basis
- is rapid, efficient and simple to perform
- is sensitive to the measured property in terms of important material and environmental factors
- is repeatable and reproducible
- is of low cost.

The intention was that the test could be used for:

- durability research
- predicting durability performance
- construction quality control.

1.3 STATEMENT OF THESIS

This thesis proposes that it is both possible and desirable to measure in the short-term a property of the surface layer of structural concrete that will assist in characterising the long-term resistance of concrete to chloride ingress. Such characterisation would allow concretes to be "indexed" in the sense of permitting engineers to classify their marine performance, and to control the quality of construction. Such an approach could also be used as a basis for payment for requisite quality achieved. The overarching objective of this approach would be to assist in improving the construction quality of run-of-the-mill marine construction. It is shown that a value of chloride conductivity, measured in a very rapid test at relatively early ages, can fulfil the above criteria.

1.4 SCOPE OF THESIS

The process of chloride corrosion of reinforcing steel, and fundamental physical principles relating to the controlling mechanisms were studied. Existing rapid chloride tests were reviewed, and one was used in an experimental programme in our laboratory. A new test was developed and verified. Suitable apparatus was designed and the test method was standardised. Test results were correlated with in-situ performance parameters.

An experimental programme was used to demonstrate the possibility of using the test for the purposes stated. The experimental programme involved testing concretes comprising 13 different cements or cement blends, varying from 20 to 60 MPa in design strength and with 1, 3, 7 or 28 days wet curing. The binders included two ordinary Portland cements (OPC), two sulphate resisting cements (SRC) of which one was a low alkali sulphate resisting cement (LASRC), a white cement, and blends of OPC with fly ash and slag. In total 36 mixes and more than 800 concrete specimens were tested. The short-term laboratory test results were correlated with long-term chloride ingress in-situ.

1.5 OUTLINE OF THESIS

Chapters 2 and 3 are literature reviews. Chapter 2 deals with the process of chloride corrosion of steel reinforcement and aims to identify the predominant controlling mechanism involved (ie. chloride diffusion). Chapter 3 deals with the fundamental scientific principles relating to the predominant controlling mechanism. The aim was to understand relationships between diffusion and conduction, since the mechanism of conduction has been used to rapidly measure diffusion properties.

Chapter 4 deals with the experimental programme. It includes a series of tests with an existing rapid chloride test, a series of trial tests used to develop the new test, and series of laboratory and site tests to verify the new test.

In chapter 5 existing rapid chloride test methods (conduction tests) are reviewed based on practical experience and fundamental scientific principles.

Chapter 6 deals with the development of the chloride conduction test in which the aim was to develop a practical and reliable test method that would test a material property that governs the rate of the predominant controlling mechanism.

Chapter 7 deals with the standardisation of the test method in which the aim was to produce a repeatable and reproducible test method.

Chapter 8 deals with long-term correlation studies in which the aim was to evaluate the use of the test in predicting long-term chloride levels.

Chapter 9 deals with the practical use of the test in engineering practice.

Chapter 10 concludes the thesis.

1.6 LIMITATIONS AND CONSTRAINTS

Durability related processes are generally long-term processes. Due to time constraints, correlations between early age chloride tests and long-term in-situ performance were based on one and two-year test results. Ideally, correlations should be based on longer-term data (10 years or more). An on-going monitoring programme has however, been put in place in order to generate longer term data.

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CHAPTER 2

CHLORIDE CORROSION OF REINFORCEMENT IN CONCRETE

2.1 INTRODUCTION

Generally, concrete structures in marine environments are more susceptible to steel reinforcement corrosion than structures elsewhere. The reason for this is the presence of chloride ions. Depending on the exposure conditions, chloride ions can enter concrete via diffusion, absorption or permeation, or a combination thereof. As soon as a certain critical level of chlorides is exceeded at the steel, corrosion becomes possible. The rate of corrosion will then depend on the availability of oxygen and water at the cathode, the resistivity of the concrete, and the ratio of the cathodic area to the anodic area.

Concrete provides resistance to chloride ingress by its physical pore structure and its chemical ability to bind chloride ions. The cover concrete quality is therefore of utmost importance (Mehta, 1988). The time before the chlorides get to the steel can vary from less than a year to more than a hundred years depending on the cover concrete quality. Suitable ways of characterising the quality of cover concrete are therefore required. Measurable material properties that can be related to one or more of the deterioration mechanisms are needed. Values for these properties could then be specified in performance-based codes.

The deterioration mechanisms involved in chloride corrosion were studied to identify the predominant controlling mechanisms. According to the thesis, material properties that govern the controlling mechanisms could then be used to characterise the durability of concrete exposed to chloride environments. These material parameters could also be used to predict the service life of structures.

2.2 DIFFERENT STAGES OF CORROSION

The corrosion process can be divided into four stages, with each involving distinct deterioration mechanisms (Tuutti, 1980). Each stage is discussed, and a graphical representation of the stages is shown in figure 2.1 (Miyagawa, 1991; Page, 1988).

1) Initiation stage:

Chloride ions enter the concrete. The ions either move through the concrete pores or through cracks and other 'macro' defects. The mechanisms include diffusion, absorption or fluid permeation. As the chloride ions move through the concrete, some are chemically or physically bound to the solid matrix. As the chloride ions in solution move deeper, the chloride concentration at the steel rises to a critical level. If the mix contained sufficient chlorides initially this stage is absent.

2) Corrosion stage:

The steel is depassivated, and corrosion begins. The rate can be very slow, depending on factors such as the resistivity of the concrete and the availability of oxygen and moisture at the cathode. The corrosion products which occupy a larger volume than the reagents cause cracks in the concrete which will eventually propagate to the concrete surface.

3) Acceleration stage:

Longitudinal cracks can appear at the concrete surface, increasing the supply of deleterious substances and thereby increasing the corrosion rate. Staining and spalling of concrete then follows. This stage can also occur without cracking in cases where oxygen is not present at the anode, provided enough oxygen is present at the cathode. This stage ends with the loss of serviceability of the structure.

4) Deterioration stage:

Severe loss in cross section of steel causing the strength to eventually drop below the ultimate strength.

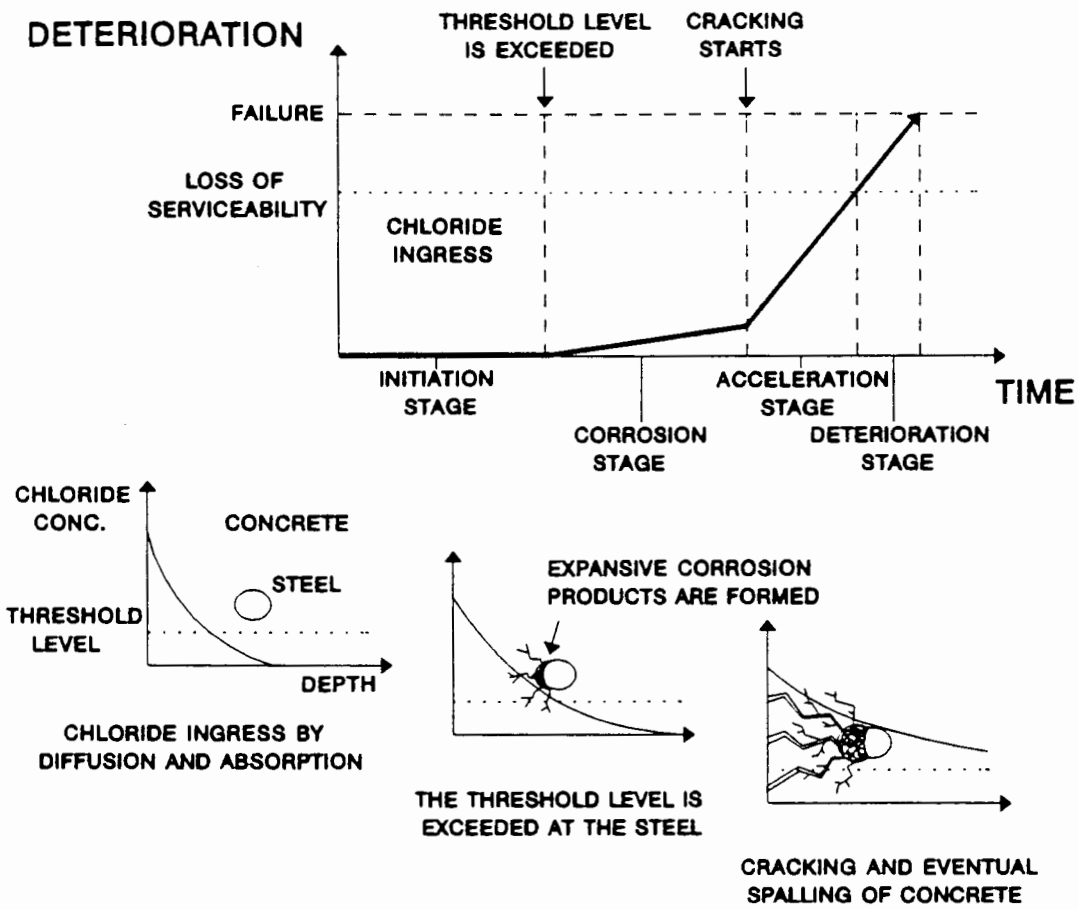

Figure 2.1: Corrosion stages.

2.3 INITIATION STAGE

2.3.1 Chloride ingress into concrete

Chloride ions are very common in marine environments. They originally come from the sea, but can also be found in the air, as wind blows spray from the sea inshore. Sea and desert sands contain chlorides, and groundwater can also be contaminated.

In colder climates, deicing salts are often used on the roads, severely affecting concrete bridges and parking garages.

Chlorides can be present in the concrete initially, referred to as internal chlorides, or

chlorides could enter concrete at a later stage, referred to as external chlorides.

Internal chlorides are contained in the mix constituents, and could originate from the following sources:

1) Admixtures.
2) Aggregates (dune sands, beach sands, sea dredged aggregates etc.).
3) Contaminated water.

External chlorides can enter concrete through the pore passages, and also through cracks and other defects (Francois and Maso, 1988; Suzuki et al, 1990). The mechanisms of chloride ingress depend on the exposure conditions and can include (see figure 2.2):

1) Diffusion:

   Occurs due to a concentration gradient of chloride ions. Diffusion can only occur through a saturated or partly saturated concrete.

2) Absorption of chloride-containing water (Kayyali, 1988) (McCarter et al, 1992):

   Occurs due to the capillary absorption of chloride-containing water into dry concrete. With repeated cycles of absorption and evaporation, surface chloride levels in concrete could be higher than that of the absorbed water, as the chloride ions are left behind by evaporation.

3) Fluid permeation:

   Water containing chloride ions could permeate through concrete under a pressure head or under gravity. Horizontal surfaces such as slabs are susceptible to this mechanism of chloride ingress.

Concrete provides resistance to these processes by means of its physical pore structure, and its chemical ability to bind chloride ions. The transport parameters through the material that can be used to characterise the physical pore structure of concrete include:

1) Steady state diffusivity, D_s
2) Water sorptivity, S
3) Gas and water permeability, k

Chloride binding is characterised by the chloride binding capacity which is a function of the chloride concentration in the pore solution.

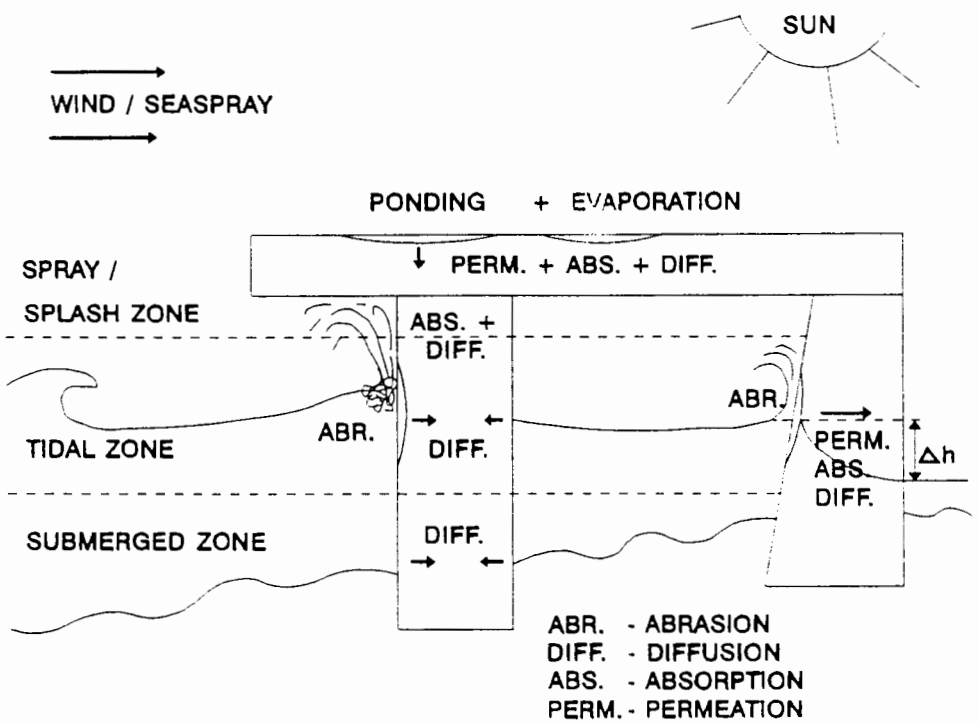

Figure 2.2: Chloride ingress in the various exposure zones.

2.3.2 Marine exposure conditions

In South Africa, chloride corrosion occurs primarily in the marine environment, since de-icing salts are not necessary in the relatively mild climate.

The environment around the concrete will influence the mechanism by which chlorides enter the concrete (Liam et al, 1992). It will also affect the availability of oxygen and water which is necessary for corrosion (see section 2.4):

1) Submerged zone:

   In the submerged zone the concrete will be saturated, and chlorides are able to enter by diffusion. The availability of oxygen is low, but the concrete conductivity is high. Corrosion can occur here if the steel is in contact with oxygen elsewhere.

2) Tidal zone:

   The exposure conditions can vary greatly in this zone. The concrete could be under water or above water for most of the time depending on whether the

member is close to the low water mark or whether it is close to the high water mark. Chlorides enter by a combination of absorption (surface layer only, 0 - 10 mm) and diffusion (see figure 2.3), but surface chloride levels cannot build up higher than that of sea-water as regular flushing with sea water occurs. Oxygen is available in this zone, and the concrete conductivity is high.

3) Splash/spray zone:

Chlorides enter through a combination of repeated absorption/evaporation at the surface (0 - 10 mm), and diffusion deeper into the concrete (see figure 2.3). In contrast with the tidal zone, the chloride concentration on the outside of the concrete could be much higher than that of the sea water, making this the worst zone for chloride ingress. Horizontal surfaces could have sea water ponding allowing permeation of chloride-containing water into the concrete by gravity. Oxygen is available. The conductivity of the concrete would depend on the level of saturation of the concrete.

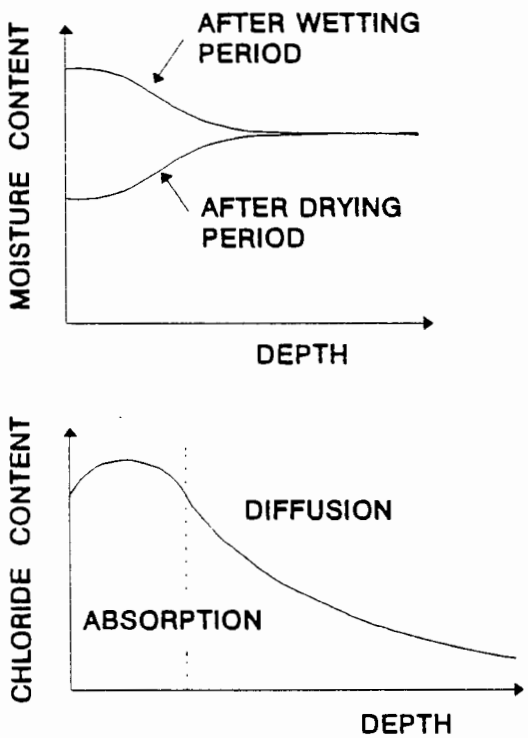

Figure 2.3: Chloride ingress via absorption and diffusion (splash zone).

4) Coastal zone:

Near the coast, the air will contain a certain amount of chlorides. Some of these chlorides deposit on concrete surfaces, and can enter the concrete with rainwater by means of absorption. This will increase the concrete conductivity and, in conjunction with carbonation, corrosion may become likely.

The orientation of the concrete member is also important. Horizontal members can have chloride solutions ponding on them, leading to rapid chloride ingress via permeation. Exposure to direct sunlight and dry winds can also increase the evaporation rate leading to a build up of concentration at the surface, thereby increasing the diffusion rate (see figure 2.2).

2.4 CORROSION STAGE

2.4.1 Corrosion process (general)

An electrochemical corrosion cell is used to illustrate the corrosion process (see figure 2.4). Corrosion takes place at the positively charged anode. The amount of current flowing is directly proportional to the rate of corrosion taking place. This current will depend on the potential difference between the cells, also known as the electromotive force (emf). It will also depend on the conductivity of electrolyte conductor, and the availability of oxygen at the cathode (Fraczek, 1987, p.16,17). The corrosion reactions are given below:

$$2Fe \Rightarrow 2Fe^{2+} + 4e^- \qquad O_2 + 2H_2O + 4e^- \Rightarrow 4OH^-$$

$$\text{Hence} \quad 2Fe + O_2 + 2H_2O \Rightarrow 2Fe(OH)_2$$

A similar process occurs as steel corrodes in concrete (see figure 2.5).

The potential difference arise from differences in surface conditions such as O_2 and salt concentrations and temperature differences. The moist concrete acts as the electrolyte

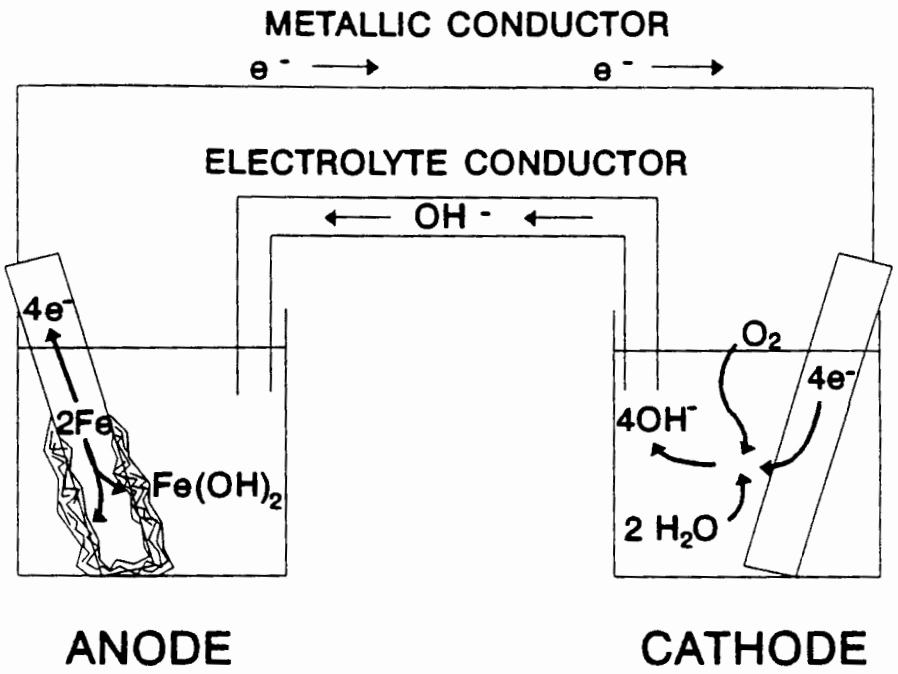

Figure 2.4: Electrochemical corrosion cell (Hime and Erlin, 1987, p. 10).

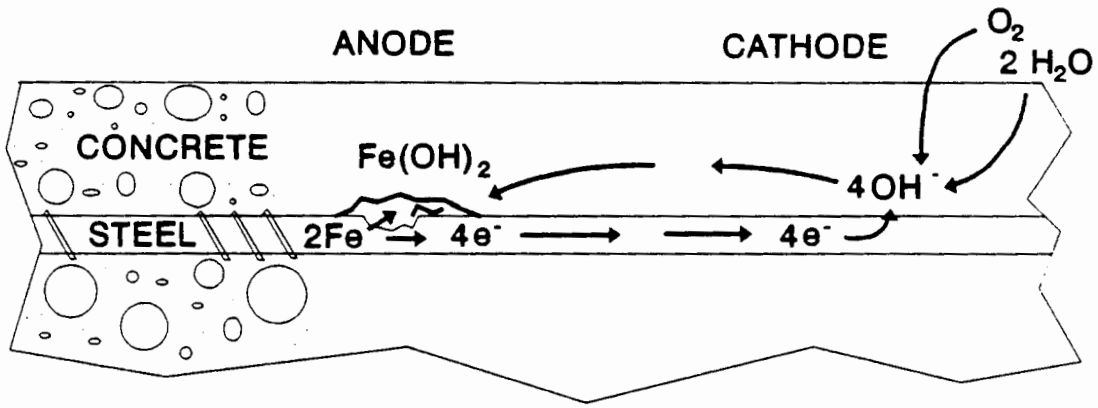

Figure 2.5: Corrosion cell in reinforced concrete (Hime and Erlin, 1987, p. 10).

conductor, and the steel as the metallic conductor. The distance between the anodes and cathodes can be a few mm (microcell), or a few meters (macrocell). Generally the cathodic area is much larger than the anodic area, and it has been found that for higher cathodic/anodic area ratios the corrosion intensity is higher (Fraczek, 1987, p.16) (Wilkins and Sharp, 1990, p.15).

For corrosion to occur the following conditions must be satisfied in addition to depassivation

(see 2.4.2):

1) Oxygen and water must be present at the cathode. Oxygen need not necessarily be available at the anode where corrosion occurs (Hime and Erlin, 1987, p.7).
2) Ions must be able to move from the cathode to the anode. This can only happen by diffusion through moist concrete.
3) The anode and cathode must be connected by a metallic conductor.

2.4.2 Passivation

In the highly alkaline concrete (pH > 12), the steel is protected by a layer of gamma iron oxide (γFe_2O_3) (see figure 2.6). This layer must be broken down or destroyed before any corrosion can occur.

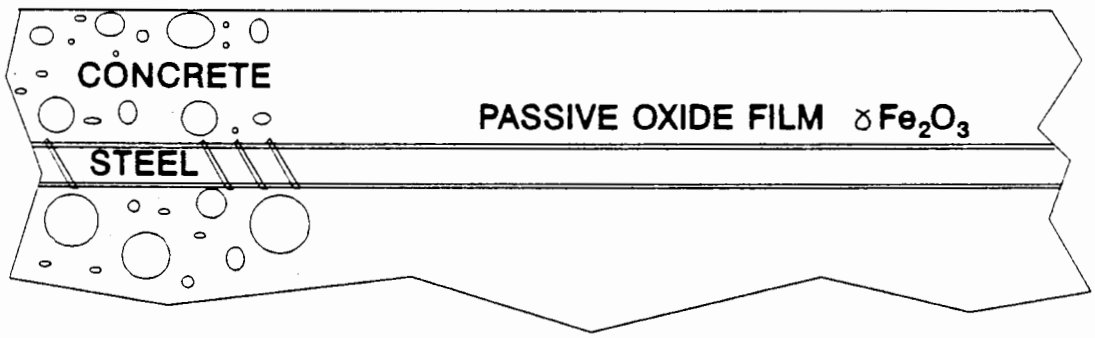

Figure 2.6: Protection of the steel by a passive oxide film.

The passivation can be destroyed by:

1) A lowering in the pH due to carbonation. General widespread corrosion may then follow, and as the corrosion products (iron oxides) have a greater volume, cracking, staining and spalling of the concrete takes place.
2) Aggressive ions such as chlorides or bromides. Localised 'pitting' corrosion may then follow, however in this case the corrosion products do not always have a much greater volume (Wilkins and Sharp, 1990, p.15), and large sections of steel can be lost before there is any visible evidence of corrosion.

In marine environments, chlorides (from the sea and seaspray) are the main cause of

depassivation. Corrosion also occurs at a far greater rate in the presence of chlorides. The mechanism by which chlorides cause depassivation is still uncertain as:

1) The addition of NaCl does not necessarily lower the pH of concrete.
(The drop in pH at the site of corrosion only occurs after corrosion has started, and occurs as a result of the corrosion reactions.)

2) Steel in concrete with high pH values has undergone corrosion in the presence of chlorides.

The following complementary explanations have been put forward:

1) Complex formation processes play a role (Hime and Erlin, 1987, p.7,8): Chloride ions release ferrous ions and react with them. This reaction transports the ferrous ions into the electrolyte.

$Fe^{2+} + 4\ Cl^- > FeCl_4^{2-}$

$Fe^{3+} + 6\ Cl^- > FeCl_6^{3-}$

The iron-chlorides then react with the hydroxide ions to produce rust.

$FeCl_6^{3-} + 2\ OH^- > Fe(OH)_2 + 6\ Cl^-$

The chloride ions are then liberated to take part in the same process again.

2) The stable γFe_2O_3 layer should be seen as a dynamic system (Alvarez and Galvele, 1984), which is constantly being broken down and repaired. In concrete without chloride ions, any opening in this layer will be repaired by the reaction of ferric ions with hydroxide ions forming the stable γFe_2O_3 layer (see figure 2.7 pt. 1). The negatively charged hydroxide ions are very mobile, and will readily diffuse to any anodic site. However, when chloride ions are present in sufficient quantities, some of the iron will react with the chloride ions. The negatively charged chloride ions are also very mobile, and would be in competition with the hydroxide ions. The difference in the second case is that the reaction products of the ferric and chloride ions are soluble, and the ferric ions will be removed from the steel surface preventing the repair of the passive layer.

At the anode the pH will drop as more chloride ions (which belong to the strong acid, HCl) are attracted electrostatically (see figure 2.7 pt. 2). At the cathode more hydroxide ions will be produced, provided enough oxygen and water are present, and the pH will remain high. This polarisation effect increases the rate of corrosion and leads to the very localised 'pitting'

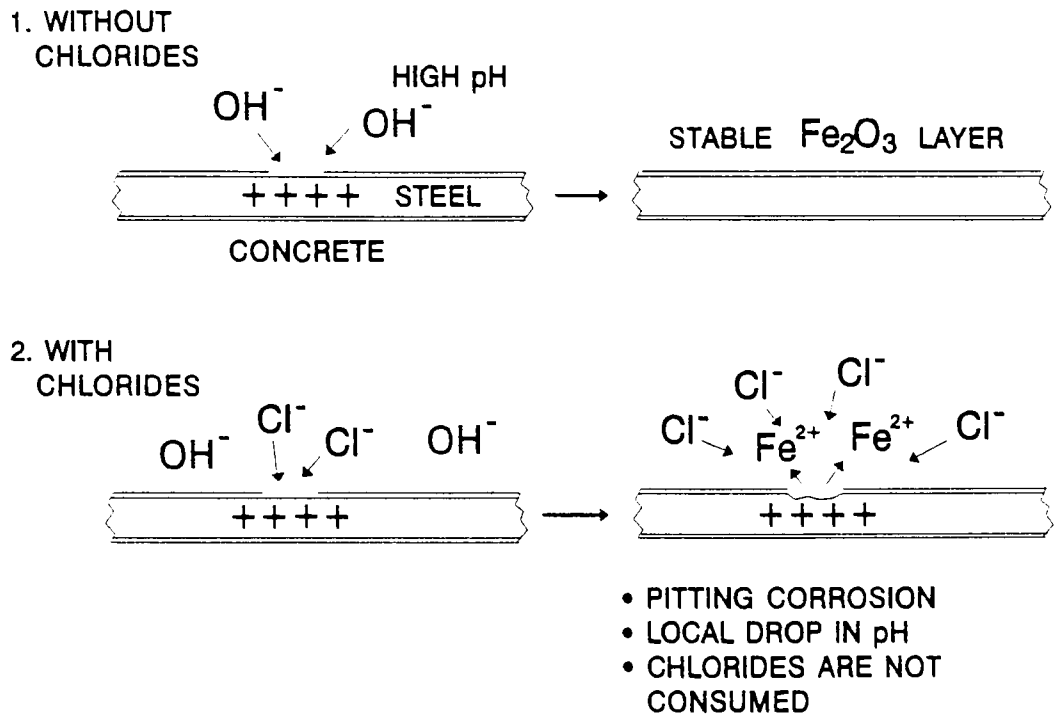

Figure 2.7: Breakdown of passive oxide film in the presence of chloride ions.

corrosion.

Localised corrosion is usually cathodically controlled, and will be most intense when driven by an extensive cathode (Wilkins and Sharp, 1990, p.15).

If chlorides are present in the pore liquid of a concrete, the conductivity of the concrete (which acts as the electrolyte conductor) will rise significantly, as chloride ions are very mobile. Differences in chloride concentrations also lead to differences in potentials along the steel.

2.4.3 Critical (threshold) chloride contents

The critical chloride content refers to the minimum chloride content needed to initiate corrosion.

In concrete some chloride ions will be bound to the solid matrix, and some will be dissolved in the pore solution (Rasheeduzzafar et al, 1991). Only the ions dissolved in the pore solution

pose a corrosion risk. It has been determined that a Cl^-/OH^- ratio above 0.6 in the concrete pore solution will initiate corrosion (Hausmann, 1967). Factors such as cement type, cement content and carbonation could affect the OH^- concentration and therefore influence the concentration of chloride ions needed to initiate corrosion.

As a general approximation the critical 'total' chloride content with respect to cement mass, or the critical 'water soluble' chloride content with respect to cement mass is more commonly used (Lewis, 1962; Clear, 1974). This is done because of the difficulty in determining the Cl^-/OH^- ratio in the pore solution.

To determine the Cl^-/OH^- ratio in the concrete pores, the porewater would need to be expressed with a porewater expression apparatus. This is usually done on pastes or mortars. The coarse aggregate in concrete is relatively hard, and the apparatus will not last very long should concrete specimens be expressed. A further problem with this method is that only small quantities of solution are expressed complicating the process of analysing the solution (Arya and Newman, 1990).

2.5 CONCLUSIONS

The time to initiation of chloride corrosion depends mainly on the rate at which chloride ions enter concrete. Chloride ions can enter concrete through the pore passages, or through cracks and other 'macro' defects. The transport mechanism involves mainly diffusion, but absorption and fluid permeation also occurs. The exposure conditions will determine the significance of the various transport mechanisms. Concrete provides resistance to these processes by means of its physical pore structure, and its chemical ability to bind chloride ions.

To achieve durable concrete would involve minimising 'macro' defects, such as cracks and honeycombing, and improving the 'micro' pore structure in terms of the relevant transport mechanisms. The philosophy is to characterise the potential durability of the material in terms of measurable material properties which are related to the mechanisms of degradation (see chapter 1). Work has already been done on characterising concrete using absorption tests, and permeability tests (Ballim, 1993).

This thesis focuses on characterising concrete in terms of its resistance to chloride diffusion. Chloride diffusion is believed to be the predominant controlling mechanism involved with chloride ingress in saturated or near-saturated concrete. A measure of the diffusivity of concrete to chloride ions would therefore be an ideal property for characterising the potential durability of concrete exposed to chloride environments.

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CHAPTER 3

CHLORIDE DIFFUSION: AN ELECTROCHEMICAL BACKGROUND

3.1 INTRODUCTION

Chloride diffusion is the predominant controlling mechanism of chloride ingress into saturated concrete from an external source. The chloride diffusivity of concrete, characterised by the chloride diffusion coefficient, D, is often used as a material parameter to characterise the resistance of concrete to chloride ingress. This parameter is also used when long-term predictions of chloride ingress into concrete are made.

Many methods have been used to determine the chloride diffusivity of concrete. These include determinations from chloride profiles (total and water soluble) for site concretes, chloride ponding tests, steady state diffusion tests and rapid chloride tests (conduction tests). Unfortunately, each test can yield a different 'chloride diffusivity' value for the same concrete, since these tests seldom isolate the mechanism of diffusion from other factors involved. Each test incorporates a variety of factors which could eventually be reflected in the measured chloride diffusivity.

Diffusion and conduction are complicated electrochemical processes influenced by factors such as ionic concentrations, temperature and the types of ions present. Diffusion coefficients are often determined at various temperatures, using ideal relationships which are only suitable at low concentrations and which exclude interactions with other ions. Determinations of diffusion coefficients also often include mechanisms other than diffusion, such as chloride binding and the movement of the pore solution due to absorption or pressure differences (ie. hydrostatic- or osmotic pressures). Diffusion determinations on concrete saturated to various degrees also differ. To complicate the process, concrete changes significantly with time as the cement continues to hydrate and carbonation and other pore blocking mechanisms occur.

This chapter explains relevant electrochemical processes in a simple way, and then continues to discuss ionic-transport through porous materials.

3.2 FACTORS AFFECTING IDEALITY IN SOLUTIONS

(Bockris and Reddy, 1970)

Most electrochemical relationships are based on ideal solutions. Electrolyte solutions in which the ions behave independently of each other are said to be ideal. In ideal solutions (low concentrations) the activity of the ionic species equals its concentration. At higher concentrations non-ideality results from ion-solvent interactions and ion-ion interactions. The implication is that at high concentrations, electrochemical relationships based on ideal solutions do not apply.

3.2.1 Ion-solvent interactions

3.2.1.1 Dissolution

When a solid ionic crystal such as NaCl is placed in a solvent such as water, the solid crystal will dissolve. Water molecules acting as electric dipoles remove the ions from the crystal by means of electrostatic forces. In the solution each ion is surrounded by a number of preferentially orientated water molecules (ion-sheath) (see figure 3.1).

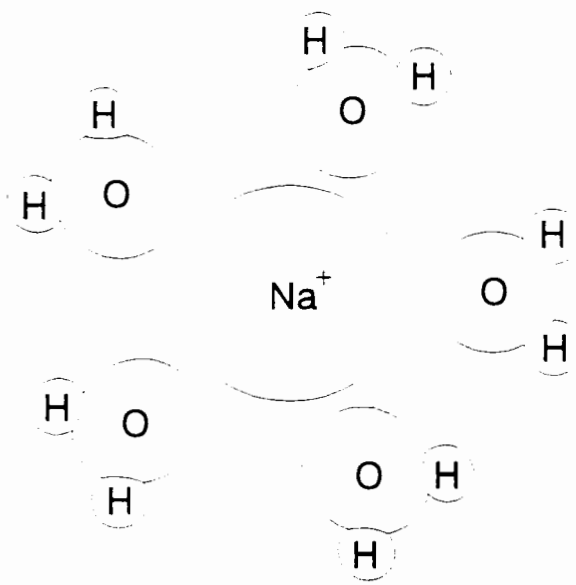

Figure 3.1: Ion sheath: water molecules around a sodium ion.

The number of molecules surrounding the ion is termed the solvation number (hydration number with water as solvent). For chloride it is 1 ± 1, and for sodium it is 5 ± 1, in

water. The lower solvation number of chloride ions results in them being more mobile than sodium ions in water.

3.2.1.2 Activity coefficient

The water molecules that are bound to ions cannot be effective in dissolving more ions. This leads to an increase in the effective ionic concentration in a solution, as the number of free water molecules are reduced. A decrease in the activity coefficient of the water results (increase in activity of ions), where the activity coefficient is a factor multiplied by the apparent ionic concentration to give the effective ionic concentration. The activity coefficients of a few NaCl solutions are shown in table 3.1:

Table 3.1: Free water and activity coefficients for NaCl solutions.

Concentration of NaCl (M)	Moles free water / litre	Activity coefficient of water
0	55.5	1.0
0.1	55	0.99665
1	48.5	0.96686
5	< 25	0.8068

The diffusion of ions is influenced by activity coefficients, since diffusion occurs under a concentration gradient. A lower activity coefficient (of the ions) will lead to a lower diffusion rate of the ions.

3.2.1.3 Dielectric constant

Since water molecules act as electrical dipoles, water is a dielectric material which can store charge. This property of a material is characterized by a dielectric constant. This constant is one for a vacuum. A dielectric medium will affect the electrostatic force between two charged ions (see equation 3.1).

$$P = \frac{q^2}{r^2} \quad in\ a\ vacuum$$

$$P = \frac{q^2}{\xi r^2} \quad in\ a\ dielectric\ medium \qquad (3.1)$$

where P ... electrostatic force (dyne)
q ... electric charge (coulomb)
r ... distance between charges (cm)
ξ ... dielectric constant (dimensionless)

The dielectric constant depends on temperature, and ionic concentrations present in the electrolyte solution (see tables 3.2 and 3.3).

The electrostatic potential of an ion in solution is equal to the work done in moving the charged ion from infinity to that point; this would clearly depend on the dielectric constant of the solvent.

The conduction of ions under an electric field is influenced by the dielectric constant of the medium. Conduction of an ionic species will be lower when the dielectric constant is lower.

3.2.2 Ion-ion interactions

At high ionic concentrations, ions cease to behave independently. These ion-ion interactions affect the equilibrium properties of ionic solutions, and they interfere with the drift of ions.

Due to the need for charge balance, each positive ion in solution will be surrounded by an ionic cloud with a net negative charge. The thickness of this cloud, called the ionic atmosphere (measured in Angstroms), depends on the concentration of ions present in the solution, and it affects the dielectric constant of the solution (Debye-Huckel theory). The dielectric constant is temperature dependant (see table 3.2), hence the dependence of solvation on temperature. Solvation is caused by electrostatic forces. These forces are stronger when the dielectric constant is lower; hence dissolution occurs more easily at higher temperatures.

Table 3.2: Dielectric constant of water at different temperatures.

Temperature (°C)	Dielectric constant, ξ
0	84.2
25	78.2
62	72.5

The dielectric constant is also dependant on ionic concentrations in the solution (see table 3.3):

Table 3.3: Dielectric constants of different solutions (25 °C).

Water and salt solutions	Dielectric constant, ξ
water	78.2
1 M NaCl	69 ± 2
2 M NaCl	60 ± 2
5 M NaCl	48 ± 2
1 M $MgCl_2$	50 ± 2

3.3 ION TRANSPORT IN SOLUTIONS

3.3.1 Diffusion

Diffusion refers to the movement of ions under a concentration gradient. Ions possess a chemical potential (different from electrostatic potential), as they are constantly moving in random directions, and bouncing off each other. To attain minimum free energy the ions will spread themselves out uniformly as they undergo these random movements. This is best described by Fick's first law for steady state diffusion (see equation 3.2).

$$J_D = - D \frac{dc}{dx} \quad (3.2)$$

where J_D ... ionic flux (mole / (cm^2.s))
D ... ion diffusivity (cm^2 / s)
dc/dx... concentration gradient (mole / (cm^3.cm))

The ion diffusivity is temperature dependent. In some cases another constant B which is independent of temperature is used. D is related to B by the following relationship:

$$D = BRT \quad (3.3)$$

where B ... diffusion coefficient independent of temp. (cm^2/J.mole.s)
R ... gas constant (J.mole / K)
T ... absolute temperature (K)

With the preceding equations ideal behaviour is assumed with the activity coefficient equal to one. For high concentration solutions (taking account of the activity coefficient) the equation becomes:

$$J_D = - D \frac{dc}{dx} \left(1 + \frac{d \ln f}{d \ln c}\right) \quad (3.4)$$

where f ... activity coefficient (dimensionless)
c ... concentration (mole)

Different ions have different diffusivities due to their different ionic radii, and solvation numbers (see table 3.4), which lead to some being more mobile.

Table 3.4: Typical ion diffusivities in water (low concentration).

Ion	Diffusivity
Na^+	1.334 10^{-5} cm^2/s
Cl^-	2.032 10^{-5} cm^2/s

For non-steady state diffusion, Fick's second law holds (see equation 3.5).

$$\frac{\partial c}{\partial t} = - D \frac{\partial^2 c}{\partial x^2} \qquad (3.5)$$

where t ... time (s)

This partial differential equation can be solved using the Laplace transformation method, and applying suitable boundary conditions.

3.3.2 Conduction

Conduction refers to the drift of ions under an electric field. An electric field is defined as the change in electrostatic potential over distance:

$$E = - \frac{d\mu}{dx} \qquad (3.6)$$

where E ... electric field (V / cm)
μ ... electrostatic potential (V)

The electrostatic potential is dependant on the dielectric constant of the electrolyte solution, while the dielectric constant is dependant on temperature, ionic type and ionic concentrations in the electrolyte.

An electric field exerts a force on a charged ion. The force P exerted on each ion in a uniform electric field would be equal:

$$P = z F E \qquad (3.7)$$

where z ... valency of ion (eq / mole)
F ... Faraday's constant (coul / eq)
zF ... charge of 1 mole z-valent ions (coul / mole)

Under an electric field, an ion would attain a net terminal velocity, termed the 'drift velocity' (v_d). The drift velocity attained under a unit electric field is defined as the mobility (u) of an ion. To determine the drift velocity of an ion under a specific electric field, the mobility is multiplied by the magnitude of the electric field. The total ionic flux (J_c) can then be determined by multiplying the drift velocity of an individual ion by the ionic concentration (c):

$$J_c = c\ u\ E = c\ v_d \tag{3.8}$$

where J_c ... ionic flux from conduction (mole / (cm^2.s))
u ... mobility of ion (cm^2 / (V.s))
v_d ... drift velocity (cm / s)

The conductivity of a material is defined as the inverse of its resistivity:

$$\sigma = \frac{L}{R\ A} \tag{3.9}$$

where σ ... conductivity (Siemens / cm)
R ... electric resistance (ohm)
L ... length of conductor (cm)
A ... cross sectional area of conductor (cm^2)

The equivalent conductance of an electrolyte is defined as the conductivity per unit charge density:

$$\Lambda = \frac{\sigma}{cz} \tag{3.10}$$

where Λ ... equivalent conductance (Siemens.cm^2.eq^{-1})
cz ... charge density (eq/cm^3)

Λ decreases at higher concentrations, due to ion-ion interactions (see table 3.5):

Table 3.5: Equivalent conductances of KCl Solutions.

Concentration KCl (M)	Λ (Siemens.cm^2.eq^{-1})
0.001	146.9
0.01	141.2
0.1	128.9

Values of Λ for ions are usually given at infinitely dilute solutions defined as Λ_0 (see table 3.6):

Table 3.6: Equivalent conductances of different ions.

Ion	Λ_0 (Siemens.cm^2.eq^{-1})
H^+	349.82
OH^-	198.5
Na^+	50.11
Cl^-	76.34

Using a simple relationship, these values can be converted to equivalent conductances at different concentrations (0 - 0.1 M):

$$\Lambda = \Lambda_0 - A\sqrt{c} \qquad (3.11)$$

where A ... constant dependant on electrolyte

For $CaCl_2$, Λ_0 = 135.7, and A = 165. At higher concentrations the change in viscosity of the solution becomes significant.

The equivalent conductance (Λ) of an electrolyte, is related to the mobility of the ions by Faraday's constant (see equation 3.12):

$$\Lambda = F\,(u_+ + u_-) \tag{3.12}$$

where u_+ ... mobility of positive ion (cm^2 / (V.s))
u_- ... mobility of negative ion (cm^2 / (V.s))

Under an electric field, the positive ions will drift towards the cathode, and the negative ions towards the anode. The current density through an electrolyte solution is the sum of movements of all the ions. The contribution of each will depend on its concentration, as well as its mobility:

$$i = \sum z_j F c_j u_j E \tag{3.13}$$

where i ... current density (amps / cm^2)

Ions with higher mobilities, and higher concentrations will carry a higher fraction of the current.

The ionic flux (J_c) due to conduction, is equal to the current density divided by the charge per 1 mole of z-valent ions (derived from equation 3.13 and 3.8):

$$J_c = \frac{i}{zF} \tag{3.14}$$

3.3.3 Ideal relationships between diffusion and conduction

3.3.3.1 Einstein relation

Einstein determined a relationship between the diffusivity, and the mobility of ions. This was done by reversing the electric field in a solution with a concentration gradient so that conduction and diffusion cancelled each other:

$$J_D + J_C = 0$$

$$-D \frac{dc}{dx} + c(x)uE = 0 \qquad (3.15)$$

(see equation 3.2 and 3.8)

If the concentration distribution c(x) is known, D can be related to u (E is the electric field applied at zero flux). Einstein determined the following relationship using Boltzmann's law for the concentration distribution.

$$u_+ = zF \frac{D_+}{RT}$$

$$u_- = zF \frac{D_-}{RT} \qquad (3.16)$$

where D_+ ... diffusion coefficient of positively charged ion

D_- ... diffusion coefficient of negatively charged ion

3.3.3.2 Nernst-Planck flux equation

Using equation 3.16, and substituting it back into the combined flux equation (3.15) the Nernst-Planck flux equation is obtained. The Nernst-Planck equation gives the ionic flux under a combination of an electric field and a concentration gradient:

$$J = \frac{D\ zF\ E(x)c(x)}{RT} - D \frac{dc}{dx} \qquad (3.17)$$

Note that the electric field (E), as well as the ion concentration (c) can be a function of distance (x).

3.3.4 Non-ideal influences on diffusion and conduction

The above relationships apply only under ideal conditions, ie. at low ionic concentrations and excluding interactions with other ions. At higher concentrations, and in the presence of other

ions, both diffusion and conduction will be affected in different ways.

3.3.4.1 Concentration influences

Both diffusion and conduction are affected by ionic concentrations (due to ion-solvent and ion-ion interactions), but the mechanisms involved differ. Higher concentrations yield higher activity coefficients, and will in the case of diffusion lead to faster diffusion rates. Activity coefficients should strictly be included in Fick's first law (eqn. 3.2 and 3.3). Higher concentrations also yield lower dielectric constants for electrolyte solutions, and will in the case of conduction lead to a lower equivalent conductance of an ionic species. At very high concentrations (1 - 5 M) the viscosities of electrolyte solutions increase significantly, thus reducing the rate of diffusion and conduction.

3.3.4.2 Influences of other ions

In any electrolyte solution the number of negative charges have to equal the number of positive charges. This *charge balance* is maintained by chemical reactions, or the drift of charges.

When two oppositely charged partner ions diffuse through an electrolyte solution, the more mobile ions will tend to diffuse faster, and separate from their oppositely charged partner ions. This leads to a potential difference, called the *diffusion potential*. To maintain a charge balance, the diffusion of the more mobile ions will be retarded and the diffusion of the less mobile ions will be accelerated. The diffusion potential could also lead to the counter diffusion of other ions (if other ions are present). Diffusion therefore depends on the type and concentration of the other ions present.

The conduction of a specific ionic species is also influenced by the type and concentration of the other ions present. The ions with the highest concentration and mobility will carry the bulk of the current flowing (see eqn. 3.13).

3.4 ION-TRANSPORT THROUGH POROUS MATERIALS

3.4.1 Diffusion (Atkinson and Nickerson, 1984)

Diffusion through a water-saturated porous medium takes place through the aqueous phase. In some cases ions from the pore solution can be adsorbed on to the solid phases (eg. chloride binding in concrete). These ions can only move by desorption into the liquid with which they are in equilibrium. For such a system it is possible to define various different diffusion coefficients and care must be taken when quoting "the diffusion coefficient" to indicate which one is being considered.

In the liquid phase the diffusion coefficient D_f is defined in the usual way,

$$J_x = -D_f \frac{dc_\ell}{dx} \tag{3.18}$$

where J_x ... ionic flux per unit area of liquid (mole / (cm^2s))

c_ℓ ... concentration in the liquid (mole / cm^3)

When the liquid is constrained by the pore structure of the porous medium we can define a similar diffusion coefficient, D_p, for diffusion within the pore liquid,

$$J_x = -D_p \frac{dc_\ell}{dx} \tag{3.19}$$

D_p is less than D_f because the diffusion paths are being constrained by the pore structure. The pores are tortuous ie. the paths are not parallel to the concentration gradient, and the paths may be very constrictive at certain points. Van Brakel and Heertjes (1974) defined the constrictivity, δ, and tortuosity, τ, parameters to describe the porous medium such that,

$$D_p = D_f \frac{\delta}{\tau^2} \tag{3.20}$$

Usually the ionic flux is described in terms of the average flux per unit area of the medium, $J_{x,m}$ (rather than the liquid) leading to another diffusion coefficient, D_s, called the steady state

diffusion coefficient,

$$J_{x,m} = -D_s \frac{dc_\ell}{dx} \tag{3.21}$$

and

$$D_s = D_f \frac{\epsilon\delta}{\tau^2} \tag{3.22}$$

where ϵ ... volume fraction of porosity

The quantity $\epsilon\delta/\tau^2$ is known as the diffusibility of the medium (Q) and is a particularly useful parameter to characterise the transport properties of a medium,

$$\frac{D_s}{D_f} = Q \tag{3.23}$$

The steady state diffusion coefficient is only an intrinsic material property in an inert (non-reacting) porous media.

3.4.1.1 Adsorption phenomena (ionic binding)

When the average concentration gradient in the liquid is replaced by the average concentration gradient in the medium, the apparent diffusion coefficient, D_a, can be defined by the equation,

$$J_{x,m} = - D_a \frac{dc_m}{dx} \tag{3.24}$$

where c_m ... average concentration over liquid and solid phases (mole/cm^3)

$$c_m = \epsilon c_\ell + (1 - \epsilon)c_s \tag{3.25}$$

where c_s ... concentration of adsorbed ions with respect to the volume of the solid matrix (mole/cm^3)

[Note that all concentration terms are expressed in moles per the relevant volume. For example the free chloride content is expressed in moles per volume of the pore liquid, the bound chloride content is expressed in moles per volume of the solid matrix, and the total chloride content in moles per volume of the medium. Researchers sometimes express some concentration terms in moles per mass ie. mole/kg, which leads to the inclusion of extra terms to convert the units. For example Sergi et al (1992) stated the free chlorides in moles/liquid volume, but stated the bound chlorides in moles/mass of the solid matrix. They therefore had to include a term (w_e) for the liquid content per unit mass of the solid matrix.]

D_a is therefore influenced by adsorption phenomena.

$$D_a = \frac{D_s}{\alpha} \tag{3.26}$$

where

$$\alpha = \frac{c_m}{c_\ell} \tag{3.27}$$

Using equations 3.25 and 3.27, we can get α in terms of ϵ and c_s/c_ℓ. The term c_s/c_ℓ is the volumetric distribution of concentration between the solid and the liquid phases and will be denoted as γ,

$$\alpha = \epsilon + (1 - \epsilon)\gamma \tag{3.28}$$

The case where γ is constant will be referred to as linear adsorption (or linear binding). The term, γ, could also be concentration dependent in which case the phenomena will be referred to as non-linear adsorption (non-linear binding).

$$\gamma = f(c_\ell) \tag{3.29}$$

With no adsorption ($\gamma = 0$), $D_a = D_i/\epsilon$, but with significant adsorption, $D_a < D_i/\epsilon$.

Adsorption phenomena will not influence the steady state ionic flux, *provided adsorption does not alter the pore structure of the material.* Adsorption will however influence the time taken until steady state diffusion is reached since adsorption does influence the ionic flux with non-steady state diffusion.

3.4.2 Non-ideal influences on ionic transport through porous materials

All the non-ideal effects which influence ionic transport in free solutions will have the same influence on ionic transport through porous materials. These effects include ionic concentrations and the presence of other ions (see sections 3.3.4.1 and 3.3.4.2). However, some non-ideal effects such as osmosis only occur in porous materials.

3.4.2.1 Osmosis (Paul, 1993)

Porous materials act to some degree as semipermeable membranes. A semipermeable membrane is a material which selectively allows the passage of water through itself but restricts the passage of dissolved solids. This could lead to the process of osmosis which would influence the apparent diffusion coefficient.

Osmosis occurs when two solutions of different TDS (Total Dissolved Solids) are separated by a semipermeable membrane, and results in the passing of water from the lower TDS solution into the higher TDS solution. The result of this is that the initially higher TDS solution becomes diluted.

When no membrane is present only diffusion will occur, ie. the dissolved substances will diffuse from the area of higher TDS to the area of lower TDS so that a uniform TDS is eventually reached.

The driving force for osmosis is the difference in the number of water molecules on either side of a semipermeable membrane. If there are dissolved solids present in the water, less water molecules will be colliding with the membrane. The salts will also collide with the membrane but won't be able to pass through. On the side without dissolved solids, more water molecules will be colliding with the membrane, and the net movement of water molecules will be from the lower TDS side to the higher TDS side.

Osmotic pressure ($P_{osmotic}$) is, therefore, a function of collisions of water molecules with the membrane, which is a function of:

1. Numbers of dissolved substances, TDS (moles/L): Increased numbers of dissolved

non-water atoms, molecules, or ions decreases the number of collisions.

2. Absolute temperature, T (K): Increased temperature increases the number of collisions.

3. Gas constant, R = 0.08206 (L.atm/K.moles)

$$P_{osmotic} = c\ R\ T \tag{3.30}$$

Osmosis is unlikely to effect rapid chloride tests due to the high rate of ionic transport, however it might influence steady state diffusion tests. Page et al (1981) and Goto and Roy (1981) studied the diffusion of NaCl through various cement pastes. In both these studies, diffusion cells with a concentrated NaCl solution on the one side (1M) and deionized water on the other were employed. Under such conditions there may have been an osmotic flow of liquid through the cement from the low concentration to the high concentration side of the cell. Atkinson and Nickerson (1984) used KI and KCl solutions in each diffusion cell to eliminate the potential for osmotic flow (KI and KCl have very similar osmotic coefficients).

3.4.3 Conduction

Measurements of electrical conductivity of specimens saturated with an aqueous electrolyte have been used in studies of the transport properties of porous rocks (Brace, 1977). This has proved useful as a rapid substitute for diffusion measurements. Provided that the solid phase is effectively an insulator, diffusion and ionic conductivity are controlled by the same processes ie. the constrictivity and tortuosity of the pore passages.

3.4.3.1 Diffusibility (Atkinson and Nickerson, 1984)

Diffusivity and mobility are linearly related by the Einstein relation (equation 3.16). It follows that the ratio of the ionic conductivity of a sample saturated with an electrolyte, σ_s, to that of the free electrolyte, σ_f, is the diffusibility of the porous medium,

$$\frac{\sigma_s}{\sigma_f} = \frac{D_s}{D_f} = Q \tag{3.31}$$

This relationship virtually eliminates the effects of non-ideality and other factors that

influence diffusion and conduction differently, since the terms in the numerator and denominator of each ratio include the same effects. Consequently the relationship holds at very high concentrations in the presence of other ions. There are however a few factors that could affect this ratio:

If the diffusing or conducting species alter the pore structure of the porous medium (through chemical reactions, physical adsorption or precipitation) the diffusibility ratio will be affected. Should the porous medium act as a semipermeable membrane, osmotic effects could influence the diffusibility ratio. Should the porous medium act as an electronegative or as an electropositive semipermeable membrane, the diffusibility ratio could also be influenced by the charge of the ionic species.

The practical implications for concrete which does react with the diffusion species (chloride ions) is that concrete does not have a characteristic diffusibility or an intrinsic chloride diffusivity since this parameter is influenced by the diffusing species. The so-called steady state chloride diffusion coefficients determined by steady state diffusion tests might include osmotic effects and the effect of an altered pore structure. Conduction tests on the other hand would exclude these effects to some degree.

3.4.3.2 Electrochemical reactions

Conductivity measurements of porous media saturated with electrolyte solutions involve electric currents through both metallic conductors (electron flow) and through electrolyte solutions (ionic flow). In the electrolyte solutions the positive ions will migrate to the cathode and the negative ions will migrate to the anode, while in the metallic conductor the electrons will flow from the anode to the cathode. At the electrodes, electron flow would have to be converted to ionic flow. This can only occur if chemical reactions take place at the electrolyte-electrode interface (see figure 3.2).

Electrochemical reactions remove electrons from the cathode, and supply electrons to the anode. Reduction reactions therefore take place at the cathode and oxidation reactions take place at the anode. These reactions also depend on the pH of the electrolyte as shown in table 3.7.

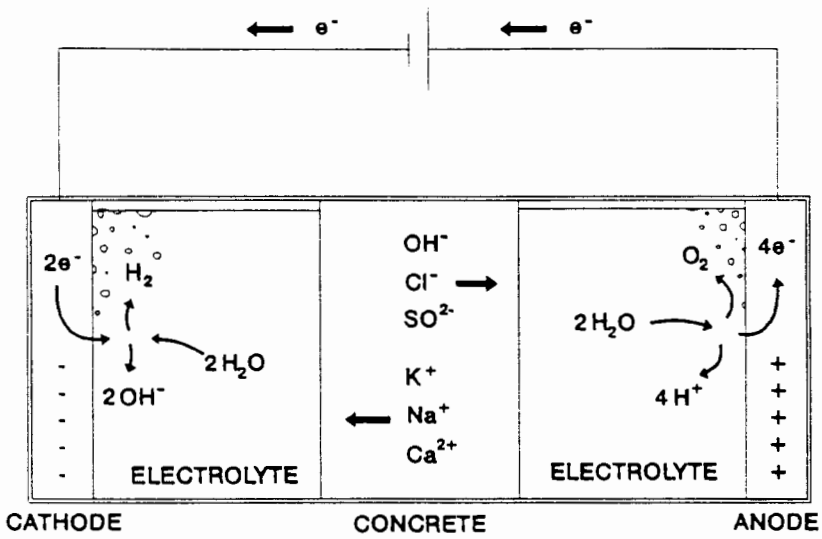

Figure 3.2: Electrochemical reactions at electrode - electrolyte interfaces.

Table 3.7: Electrochemical reactions.

		Cathode		Anode
pH > 7	1	$2H_2O + 2e^- \Rightarrow H_2 + 2OH^-$	2	$4OH^- \Rightarrow 2H_2O + O_2 + 4e^-$
pH < 7	3	$2H^+ + 2e^- \Rightarrow H_2$	4	$2H_2O \Rightarrow O_2 + 4H^+ + 4e^-$
			5	$2Cl^- \Rightarrow Cl_2 + 2e^-$

There will be a drop in electric potential over the electrode-electrolyte interface due to these reactions (see figure 3.3). The potential drop at this interface will increase if the concentrations of the reaction products increase and the concentrations of the reagents decrease. This phenomenon is referred to as polarization resistance and can be eliminated by using a.c. currents. Alternatively, the effect of the polarization resistance on the measured current can be eliminated by measuring the potential difference across the porous sample and then adjusting the applied voltage to keep the potential difference across the sample constant.

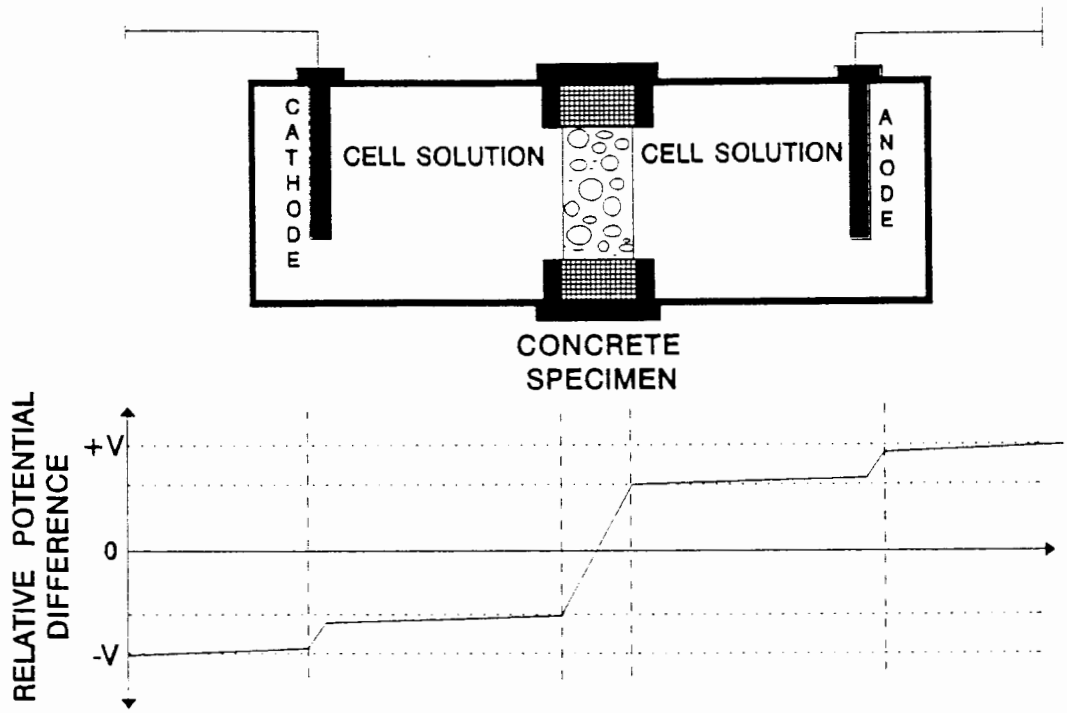

Figure 3.3: Potential drops over various sections associated with conduction tests.

3.5 CONCLUSIONS

Diffusion refers to the movement of ions under a concentration gradient. The rate of diffusion is characterised by a diffusion coefficient, D, and is equal to the ionic flux under a unit concentration gradient. At a constant temperature, and at low concentrations each ion would have a characteristic diffusivity, but the presence of other ions and higher concentrations would affect this diffusivity.

Conduction refers to the movement of ions under an electric field. The rate of conduction is characterised by conductivity, σ, and is equal to the charge flux (current density) under a unit electric field. At a constant temperature, and at low concentrations each ion would have a characteristic equivalent conductance (conductivity per unit charge). The presence of other ions and higher concentrations would affect this equivalent conductance.

At low concentrations diffusivity and equivalent conductances are linearly related by the Einstein relation.

Ionic diffusion and conduction occur much slower through porous materials because of the tortuosity, porosity and constrictivity of the pores. The extent to which these factors reduce the diffusivity and conductivity of specific ions is characterised by the diffusibility of the material which is the ratio between the transport coefficients in the material to the transport coefficients in water.

$$Q = \frac{D_s}{D_f} = \frac{\sigma_s}{\sigma_f}$$

This is a particularly useful material parameter as it is much less sensitive to non-ideal effects and holds at high concentrations. Using this relationship, diffusion coefficients can be determined using simple conduction tests.

For free solutions, porous materials, and porous materials with adsorption (binding) characteristics, various different diffusion coefficients can be defined:

D_f ... Diffusion coefficient through free water: Concentration gradient in liquid, ionic flux through liquid.

D_p ... Diffusion coefficient through porous material: Concentration gradient in liquid, ionic flux through liquid.

D_s ... Steady state diffusion coefficient: Concentration gradient in liquid, ionic flux through medium (inert medium).

D_a ... Apparent diffusion coefficient: Concentration gradient in medium, ionic flux through medium.

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CHAPTER 4

EXPERIMENTAL DETAILS

4.1 INTRODUCTION

The experimental programme consisted of trial tests, and two series of tests (series 1 tests and series 2 tests). The series 1 tests involved the use of the Dundee rapid chloride test (see section 5.5). The possibility of developing an improved rapid chloride test was realised during this series of tests (chapters 5 and 6). Trial tests were then conducted to develop the new rapid chloride test. This was followed by the series 2 tests which involved the use of the new chloride conduction test (chapters 6 and 7).

The series 1 and 2 tests included correlations between laboratory test results and in-situ test results (chapter 8). Although the series 1 tests involved the use of the Dundee rapid chloride test, these correlations are relevant to this thesis since the test essentially measures the same property as the new test developed. The correlations also involved longer term results (2 years instead of 1 year), which is of additional value.

Both series of tests formed part of industrial research projects: each with different but complementary objectives to those of this thesis. The focus of the industrial projects was on the marine durability performance of a range of cement based products, while the focus of this thesis was on the development of a new rapid chloride test and its use in engineering practice.

The discussions of test results directly relevant to the objectives of this thesis is included in the main body of the thesis, while the discussions of test results relevant to the objectives of the industrial research projects are included in the appendix. Note that the portions in the appendix relate indirectly to the second objective of the thesis ie. the use of the chloride test in engineering practice (chapter 9). The full set of test results for series 1 and 2 tests are also included in the appendix.

The purpose of the series 1 and series 2 tests necessitates very detailed experimental information with regards to the materials used. These details are all presented in this chapter. In contrast, the trial tests focus on the test apparatus and test method and do not generally require very detailed information on materials used. The trial tests also do not consist of one

homogeneous series of tests, but rather of a number of different and separate tests. The details for these tests are therefore discussed in the relevant chapters (chapter 6 and 7). In some instances, samples used in the series 2 tests were also used in the trial tests.

4.2 SERIES 1 TESTS

The series 1 tests was part of an industrial research project performed at the University of the Witwatersrand (WITS) and the University of Cape Town (UCT). The objective of this project was to study the marine durability properties of various CSF concretes. The mixes and samples were prepared at WITS and most of the experimental information provided in this section is extracted from the report prepared by Ananmalay (1996).

4.2.1 Mixes tested

The series of tests involved 21 concrete mixes varying from 25 to 75 MPa in design strength (see table 4.1). The binders included an ordinary portland cement and blends with densified condensed silica fume (DCSF) and undensified condensed silica fume (UCSF).

Table 4.1: Mix details and numbers; series 1 tests.

BINDER TYPE	NOMINAL STRENGTH		
	25 MPa	**50 MPa**	**75 MPa**
OPC	**B1**	**B2**	**B3**
OPC - 5% UCSF	**B4**	**B5**	B6
OPC - 10% UCSF	**B7**	B8	B9
OPC - 15% UCSF	B10	B11	B12
OPC - 5% DCSF	**B13**	**B14**	B15
OPC - 10% DCSF	**B16**	B17	B18
OPC - 15% DCSF	B19	B20	B21

Where OPC represents 'ordinary portland cement', UCSF represents 'undensified condensed silica fume' and DCSF represents 'densified condensed silica fume'. Due to time constraints, only the mixes in bold were tested using the Dundee rapid chloride test. All the mixes were

tested in the in-situ tests.

4.2.3 Materials used

4.2.3.1 Aggregates

Dolerite 19 mm stone and Dolerite crusher sand were used in all the mixes. Both aggregates were obtained from the Ngagane Quarry near Newcastle, KwaZulu Natal. Table 4.2 shows the density properties of the aggregates and table 4.3 shows the grading analysis of the dolerite crusher sand.

Table 4.2: Density properties of sand and stone

	19mm Stone	Crusher Sand
Relative Density	2.97	2.84
Compacted Bulk Density (kg/m^3)	1560	1880
Loose Bulk Density (kg/m^3)	1470	1700

Table 4.3: Grading analysis of dolerite crusher sand.

Sieve size (um)	**% Retained**	**% Passing**	**Cumulative % retained**
6700	3.1	96.9	3.1
4750	17.2	79.7	20.3
2360	31.8	47.9	52.1
1180	24.4	33.5	66.5
600	8.2	25.3	74.7
300	5.7	19.6	80.4
150	4.9	14.7	85.3
75	4.3	-	-
<75	10.4	-	-
TOTALS	100	-	382.4

4.2.3.2 Cement and cement blends

The OPC used in this investigation was obtained from the Dudfield factory of Anglo Alpha and complied with SABS 471-1971. Fifty standard pockets (50 kg) were randomly selected from a single day's production for the project. From each of the pockets, a small quantity of cement was removed and the balance stored in air-tight drums. Anglo Alpha performed chemical analyses on samples of the cements (see table 4.4). From the chemical analysis the Bogue composition was determined (see table 4.5).

Table 4.4: Chemical composition of cement.

ELEMENTS (expressed as oxides)	**PERCENTAGE (by mass)**
SiO_2	22.78
Al_2O_3	4.16
Fe_2O_3	2.54
CaO	64.33
MgO	1.45
K_2O	0.27
TiO_2	0.31
SO_3	1.84
Mn_2O_3	0.13
V_2O_5	0.01
LOI	1.58
Free Lime	1.10
P_2O_5	0.17

Table 4.5: Potential compound composition of cement.

COMPOUND	PERCENTAGE
C_3S	47.3
C_2S	29.4
C_3A	6.7
C_4AF	7.7

The UCSF and DCSF was obtained from the Witbank Anglo Alpha plant. A chemical analysis of the CSF (UCSF and DCSF were identical chemically) is shown in table 4.6.

Table 4.6: Chemical composition of CSF.

ELEMENTS (expressed as oxides)	PERCENTAGE (by mass)
SiO_3	90.89
Al_2O_3	1.58
Fe_2O_3	1.55
CaO	0.41
MgO	0.60
K_2O	0.99
Mn_2O_3	0.02
P_2O_5	0.09
V_2O_5	0.01
LOI	3.05

4.2.4 Mix proportions

The mix designs are shown in table 4.7. To ensure similar workabilities, the mixes were designed to have a slump of 40-70 mm and 30 - 60 mm for the OPC only and the CSF blended mixes respectively. The admixture used was a liquid FOSROC Conplast 430 superplasticizer.

Table 4.7: Mix proportions (per m^3) for final mix designs (OPC and UCSF blends).

Binder Type	Mix No.	w/c	Water (l)	OPC (kg)	UCSF (kg)	DCSF (kg)	Stone (kg)	Sand (kg)	Admix (l)	% Admix	Slump (mm)
OPC	B1	0.80	205	256	-	-	1100	1012	-	-	55
	B2	0.53	205	390	-	-	1100	887	-	-	50
	B3	0.36	205	574	-	-	1100	714	3.134	0.55	70
OPC + 5% UCSF	B4	0.87	205	224	12	-	1100	1026	-	-	50
	B5	0.56	205	351	18	-	1100	898	-	-	35
	B6	0.39	205	497	26	-	1100	750	2.197	0.42	60
OPC + 10% UCSF	B7	1.00	205	185	21	-	1100	1051	-	-	45
	B8	0.61	205	304	34	-	1100	919	-	-	45
	B9	0.43	205	424	47	-	1100	788	1.978	0.42	55
OPC + 15% UCSF	B10	1.00	205	174	31	-	1100	1046	-	-	50
	B11	0.61	205	288	51	-	1100	911	2.326	0.69	60
	B12	0.43	205	401	71	-	1100	777	3.568	0.76	60
OPC + 5% DCSF	B13	0.91	205	214	-	11	1100	1036	-	-	50
	B14	0.59	205	331	-	17	1100	917	-	-	55
	B15	0.41	205	447	-	25	1100	769	-	-	45
OPC + 10% DCSF	B16	0.91	205	203	-	23	1100	1031	-	-	40
	B17	0.59	205	314	-	35	1100	909	-	-	50
	B18	0.43	205	424	-	47	1100	788	1.837	0.39	55
OPC + 15% DCSF	B19	0.91	205	192	-	34	1100	1025	0.633	0.28	50
	B20	0.59	205	296	-	52	1100	901	1.462	0.42	50
	B21	0.43	205	401	-	71	1100	777	3.162	0.67	55

4.2.5 Curing

The curing conditions were:

a) Standard wet curing: The samples were demoulded after 24 hours and then placed in a curing tank at 23 °C. Wet curing periods were 1, 3, 7 or 28 days (which included the first 24 hours).

b) Dry curing in controlled laboratory conditions.
This involved exposing specimens to a 23 °C, 60 % RH laboratory environment after the periods of wet curing given in a). This applied to the durability characterization tests (ie. rapid chloride, oxygen permeability and water sorptivity tests), and the direct durability tests (outdoor exposure blocks). (Note that a standard 28 day wet curing was included in this option.)

4.2.6 Laboratory test methods

The tests performed in the industrial research project included a modified version of the Dundee rapid chloride test (see section 5.5), the oxygen permeability test and the water sorptivity test (see series 2 tests for the permeability and sorptivity test methods). Only the work relating to the Dundee rapid chloride test was regarded as relevant to this thesis. The details regarding the test method are discussed in chapter 5.

4.2.7 In-situ tests (Chapter 8)

These tests involved placing concrete samples in a marine exposure zone in Simonstown in the Cape Peninsula, and determining chloride ingress profiles (acid soluble) after 2 years. This will be repeated after 4 and 8 years. Apparent chloride diffusivities can be inferred from these profiles using Fick's Second Law. The chloride indexes determined from the laboratory tests can then be correlated to these values, taking account of the additional variables such as chloride binding and exposure conditions.

The exposure site was located in Simonstown harbour under one of the jetties. The site had the following characteristics:

(a) Little wave action (reducing abrasion).
(b) No direct sunlight.
(c) Sheltered from rain.

Three tidal zones were chosen:

(a) Submerged zone (just below spring low tide).
(b) Mid-tidal zone.
(c) Upper-tidal/spray zone (under water only during spring high tide).

The concrete cubes were placed in wooden cages (Meranti/PVC construction). Two cage sizes were used; the larger could house 16 cubes and the smaller one 8 cubes (see figure 4.1).

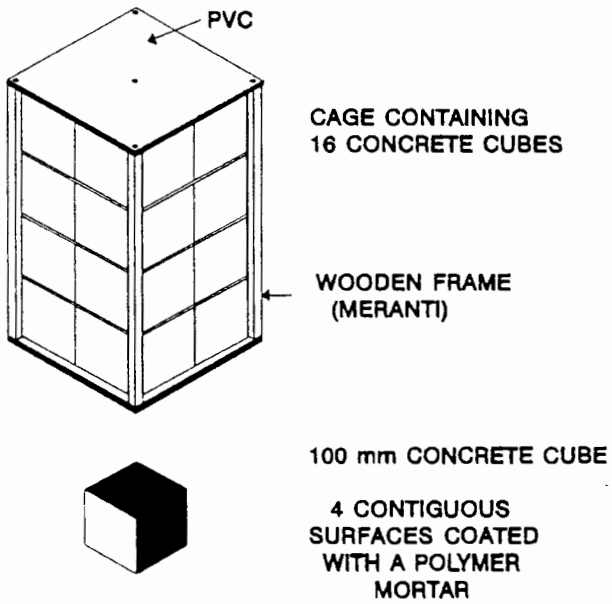

Figure 4.1: Wooden cage containing on-site exposure cubes.

The cages were placed in the exposure site in April 1993, and chloride penetration profiles were determined after 2 years (1995). Future chloride profiles will be measured after 4 years (1997) and 8 years (2001).

The in-situ exposure test was used to test all the mixes (mix 1 - 21, 3 cubes per mix) wet cured for 3 days.

The first set of exposed cubes was transported to the laboratory after 2 years exposure, and the chloride profiles were determined. This was done by drilling three 20 mm diameter holes in each cube. The depth increments depended on the concrete grade:

25 MPa - 4 x 20 mm depth increments

50 MPa - 4 x 15 mm depth increments

75 MPa - 4 x 10 mm depth increments

The total chloride contents were determined in accordance with BS1881, using a Mettler auto-titrator. The percentage total chloride content with respect to cement mass was calculated.

4.3 SERIES 2 TESTS

4.3.1 Mixes tested

This series of tests involved testing 36 concrete mixes varying from 20 MPa to 60 MPa in design strength, and using two different coarse aggregates - greywacke and granite (see table 4.8). In all, 13 different cements or cement blends were used. The objective of the industrial research project was to determine the influence of C_3A levels, Alite/Belite ratios and the addition of mineral extenders (fly ash and slag) on marine durability performance in terms of chloride ingress.

The binders included two ordinary portland cements (OPC), two sulphate resisting cements (SRC) of which one was a low alkali sulphate resisting cement (LASRC), a white cement, and blends of OPC with fly ash and slag. The names of the source factories (De Hoek - D.H., Riebeeck West - R.W., Slurry) were assigned to the OPC and SRC cements. The pure cement mixes included Slurry SRC, De Hoek OPC, Riebeeck West LASRC, Riebeeck West OPC and White cement. The cement blend mixes included 30 % and 50 % fly ash mixes, and 50 % and 70 % slag mixes, blended with either Riebeeck West OPC or De Hoek OPC.

The cements were homogenised and stored in 25 ℓ air tight drums by PPC (Pretoria Portland Cement Company). These were delivered to and stored at the Portland Cement Institute laboratory in Goodwood, Cape, where the mixing and casting were done. Twenty four hours after casting, the concrete specimens were demoulded and transported to UCT where they were cured.

From each mix thirty nine 100 mm cubes and one 300 x 300 x 500 mm block were cast. Three batches (A, B and C) were required per mix and the cubes included a reference to the particular batch. Twenty-eight cubes were cast from batch A and eleven cubes were cast from batch B. The block was cast from batches B and C, thus making the batches of similar volume.

Twelve cubes were used for the compression tests, nine for the durability index tests, six for the carbonation tests and the remaining twelve were kept for possible long-term tests. The

nine cubes for the durability index tests were cored at 28 days using a 68 mm diameter diamond tipped core barrel. Surface slices, 25 mm thick, were cut from the cores using a diamond saw.

Table 4.8: Mix details and numbers; series 2 tests.

Cement type	Mix numbers			
	Target strengths and coarse aggregate type			
	20 MPa	40 MPa	40 MPa	60 MPa
	Greywacke	Greywacke	Granite	Granite
Slurry SRC	1; 22	2	3	insufficient cement
De Hoek OPC	4	5	6	7
Riebeeck West LASRC	8	9	10	11
Riebeeck West OPC	12	13	14	15
30 % fly ash 70 % R.W. OPC	16	17	-	18
50 % fly ash 50 % R.W. OPC	19	20	-	21
30 % fly ash 70 % D.H. OPC	-	23	-	-
50 % fly ash 50 % D.H. OPC	-	24	-	-
50 % slag 50 % R.W. OPC	25	26	-	27
50 % slag 50 % D.H. OPC	-	28	-	-
70 % slag 30 % D.H. OPC	-	29	-	-
White cement	30	31	32	33
70 % slag 30 % R.W. OPC	34	35	-	36

Not all combinations of mixes were tested, as can be seen from the blank spaces in table 4.8. This was due to time constraints.

4.3.2 Materials Used

4.3.2.1 Fine Aggregate

Macassar dune sand was used for all the mixes. PCI Western Cape analyzed the fine aggregate, and the following results were obtained:

Relative density (BS 812 Part 2): 2.61
Bulk densities (BS 812 Part 2 & SABS TM 845): 1420 kg/m^3 (LBD)
1580 kg/m^3 (CBD)
Voids content (SABS TM 845): 40 %
Sieve analysis (SABS TM 845): F.M. = 2.25
The sieve analysis is shown in table 4.9.

Table 4.9: Sieve analysis (sand).

Sieve aperture (mm)	Cumulative % passing
4.750	100
2.360	94
1.180	83
0.600	58
0.300	31
0.150	9
0.075	2.8

Indicator tests for sulphates and chlorides in the sand were also conducted, but found to be negative.

4.3.2.2 Coarse Aggregates

Crushed greywacke stone (19 mm) from the Peninsula Quarry was used for the 20 MPa and 40 MPa mixes, and crushed granite stone (19 mm) from the Rheebok Quarry for the 40 MPa and 60 MPa mixes. Granite was used for the higher strength mixes to avoid alkali silica reaction. PCI analyzed the coarse aggregates and the following results were obtained:

		Greywacke	Granite
Relative density (BS 812 Part 2):		2.72	2.63
Bulk densities	LBD	1330 kg/m^3	1290 kg/m^3
(BS 812 Part 2 & SABS TM 845):	CBD	1430 kg/m^3	1380 kg/m^3
Voids content:		48 %	48 %
	Dust content	0.4 %	0.7 %
Sieve analysis (SABS TM 845):	F.M.	8.85	9.15

The sieve analyses are shown in table 4.10.

Table 4.10: Sieve analysis (stone).

Sieve aperture (mm)	Greywacke Stone	Granite Stone
	Cumulative % passing	
26.5	100	100
19.0	90	78
13.2	21	4
9.5	2	1
6.7	1	1
4.75	0.5	0.8

4.3.2.3 Cements and Cement Blends

PPC performed standard tests on samples of all the cements and cement blends.

Tests:
- Density
- Specific surface
- Standard consistency
- Setting time
- Soundness (Le Chatelier Expansion)
- Residues
- False set
- ISO (Cement mortar prism)
- VMC (Cement mortar cubes)
- BS 12

The results of these tests are contained in Appendix 2 Part B. All the cements complied with the relevant South African standard specifications.

Table 4.11 contains the specific surface areas of the Portland cements.

Table 4.11: Specific surface.

Cement type	Slurry SRC	LASRC	Riebeeck West OPC	De Hoek OPC
Specific surface (SABS 748) (cm^2/g)	4500	3000	2900	2700

The Slurry SRC cement has a substantially higher specific surface area. A high surface area increases the rate of hydration as there is greater area of contact between the cement minerals and the water (Fulton, 1986).

PPC performed chemical analyses on samples of the cements and cement blends. Tables 4.12 and 4.13 contain a summary of these results:

Table 4.12: Chemical analyses of cements.

%	De Hoek OPC	Slurry SRC	Riebeeck West OPC	LASRC
SiO_2	21.1	22.0	20.9	22.1
Al_2O_3	3.2	3.0	3.8	2.8
Fe_2O_3	3.6	4.5	3.3	4.9
Mn_2O_3	0.1	0.2	0.1	0.1
TiO_2	0.2	0.7	0.2	0.2
CaO	64.4	64.1	64.6	65.6
MgO	1.1	2.0	0.9	0.7
P_2O_5	0.1	0.1	0.1	0.1
Cl	0.0	0.0	0.0	0.0
SO_3	2.5	1.7	1.8	2.1
K_2O	0.4	0.2	0.5	0.3
Na_2O	0.3	0.1	0.2	0.1
Equivalent Na_2O	0.6	0.2	0.5	0.3
LOI	3.0	1.6	3.4	0.9
Total	100.0	100.2	99.8	99.9

Table 4.13: Chemical analyses of blends.

%	RW30FA	RW50FA	DH30FA	RW50SL	DH50SL	DH70SL
SiO_2	30.6	36.0	30.0	27.7	28.6	31.1
Al_2O_3	13.2	20.0	11.9	9.7	9.8	12.1
Fe_2O_3	3.4	3.7	3.5	2.0	1.9	1.4
CaO	46.2	34.1	47.8	49.7	48.4	42.6
SO_3	1.4	1.0	1.7	2.4	2.6	2.7
K_2O	0.5	0.5	0.4	0.7	0.7	0.8
Na_2O	0.3	0.2	0.3	0.3	0.3	0.3

Bogue analyses of the cements were calculated by PPC. The Bogue analyses are shown in table 4.14. LASRC had the lowest alumina content and the highest Alite/Belite (C_3S/C_2S) ratio. A higher Alite/Belite ratio increases the rate of hydration (Fulton, 1986).

Table 4.14: Potential compound composition of cement.

%	C_3S	C_2S	C_3A	C_4AF	C_3S/C_2S
Slurry SRC	51.1	24.0	1.9	14.3	2.13
De Hoek OPC	53.1	20.0	2.8	11.1	2.66
Riebeeck West OPC	51.7	20.5	4.8	10.3	2.52
R.W. LASRC	63.3	15.1	0.0	15.2	4.19
White cement	62.6	23.6	4.5	1.5	2.65

The different specific surface areas and Alite/Belite ratios of the Portland cements are likely to complicate the process of identifying the influence of C_3A content on durability properties.

4.3.2.4 Other mix ingredients

Water: Tap water

Superplasticizer: Conplast 430 (Fosroc)

Conplast 430 is a liquid-based superplasticizer with a water content of 60 % by volume. It is a synthetic plasticizer derived from sulphonated naphthalene and complies with BS 5075 : Part 3 and ASTM C494 as a class F High Range Water Reducing Admixture. It contains no calcium chloride.

4.3.3 Mix proportions

The mix designs are shown in table 4.15. The mixes were designed to have a slump of 50 mm (target range 30 - 80 mm). The measured slump is shown in column 10 of table 4.15. Note that the "c" in w/c ratio refers to the total binder content.

All the 60 MPa mixes contained a liquid FOSROC Conplast 430 superplasticizer. Mixes 7, 11, 15, 27, 33 and 36 contained 2.0 %, and mixes 18 and 21 contained 2.9 % and 4.0 % superplasticizer respectively, by mass of the binder in the mix. The water content of the superplasticizer was not included in "w".

Table 4.15: Mix designs.

(1) Mix no.	(2) Targ. (MPa)	(3) w/c	(4) Water (ℓ)	(5) Cement (kg)	(6) Fly ash (kg)	(7) Greywacke stone (kg)	(8) Granite stone (kg)	(9) Sand (kg)	(10) Slump (mm)
1	20	0.85	200	236		1080		856	60
2	40	0.56	190	342		1080		794	50
3	40	0.56	195	351			1040	777	65
4	20	0.83	200	240		1080		852	50
5	40	0.54	200	370		1080		744	70
6	40	0.54	200	370			1040	748	70
7	60	0.36	150	420			1040	838	50
8	20	0.87	195	224		1080		878	40
9	40	0.61	195	322		1080		797	55
10	40	0.61	195	322			1040	802	60
11	60	0.42	160	384			1040	841	95
12	20	0.83	200	240		1080		852	60
13	40	0.56	195	351		1080		773	60
14	40	0.56	195	351			1040	777	70
15	60	0.33	160	480			1040	761	80
16	20	0.76	185	171	73.3	1090		873	55
17	40	0.48	180	265	113	1090		772	55
18	60	0.30	138	320	137		1038	799	70
19	20	0.63	175	140	140	1080		874	60
20	40	0.40	175	219	219	1080		737	50
21	60	0.28	127	227	227		1019	819	80
22	20	0.71	200	280		1080		819	65
23	40	0.44	173	273	117	1118		721	75
24	40	0.36	180	248	248	1130		622	70
					(6) Slag (kg)				
25	20	0.83	185	111	111	1130		823	55
26	40	0.56	185	167	167	1130		716	70
27	60	0.38	150	199	199		1050	791	

table 4.15 - continued

(1) Mix no.	(2) Targ. (MPa)	(3) w/c	(4) Water (ℓ)	(5) Cement (kg)	(6) Fly ash (kg)	(7) Greywacke stone (kg)	(8) Granite stone (kg)	(9) Sand (kg)	(10) Slump (mm)
28	40	0.53	182	173	173	1098		790	80
29	40	0.46	182	120	281	1110		729	60
30	20	0.91	179	197		1080		943	30
31	40	0.69	164	237		1080		949	55
32	40	0.69	165	239			1040	949	45
33	60	0.53	140	286			1040	991	70
34	20	0.67	170	77	179	1080		868	
35	40	0.46	170	112	262	1148		844	60
36	60	0.30	150	150	350		1130	674	75

Mixes 18 and 21 required more superplasticizer to achieve an acceptable slump. Ideally the superplasticizer content should have been kept constant, and the water content of the mix increased since the water contents of these mixes were relatively low.

4.3.4 Curing

Different curing regimes were required for the various tests. The durability characterization tests (ie. chloride conductivity test, oxygen permeability and water sorptivity test) and the carbonation and cube compression tests required using a full scope of curing regimes. The outdoor exposure tests used only one curing regime. The curing regimes for the different tests are presented in table 4.16.

The curing conditions were:

a) Standard wet curing: The samples were demoulded after 24 hours and then placed in a curing tank at 23 °C. Wet curing periods were 1, 3, 7 or 28 days (which included the first 24 hours).

b) Dry curing in controlled laboratory conditions.

This involved exposing specimens to a 23 °C, 60 % RH laboratory environment after the periods of wet curing given in a). (Note that a standard 28 day wet curing was included in

this option.)

Table 4.16: Curing regimes.

Cube compression tests	Durability characterisation	Outdoor exposure blocks
At 3, 7, 28, 90 days wet curing.	1,7,28 days wet curing, tested after 28 days.	3 days wet curing followed by storage in RH room (2-5 months), then in exposure zone, to be tested after 1, 2 4 and possibly 8 years in exposure zone.

The outdoor exposure blocks were taken to the marine site at Simonstown in groups of twelve ie. they were in the controlled laboratory for varying periods of time (2 - 5 months). This had to be done since it would have been impractical to transport one block each week to the marine site 40 km from the University.

4.3.5 Casting sequence

The casting sequence is shown in table 4.17. The first mix was cast on 31 August 1993 and the last mix on 3 July 1995 (mix 34). Mix 34 was a repeat mix, hence the delay in casting of this mix.

Table 4.17: Casting sequence.

Mix no.	Casting date (day/month/year)	Mix no.	Casting date	Mix no.	Casting date	Mix no.	Casting date
1	31/8/93	10	1/11/93	19	14/3/94	28	18/7/94
2	7/9/93	11	8/11/93	20	21/3/94	29	25/7/94
3	14/9/93	12	24/1/94	21	28/3/94	30	1/8/94
4	20/9/93	13	31/1/94	22	11/4/94	31	8/8/94
5	27/9/93	14	7/2/94	23	18/4/94	32	15/8/94
6	4/10/93	15	14/2/94	24	25/4/94	33	22/8/94
7	11/10/93	16	21/2/94	25	2/5/94	34	3/7/95
8	18/10/93	17	28/2/94	26	4/7/94	35	19/9/94
9	25/10/93	18	7/3/94	27	11/7/94	36	3/10/94

4.3.6 Laboratory tests

The test results are discussed in Appendix 2 Part A in terms of the objectives of the industrial research project. The full set of test results are included in Appendix 2 Part B.

4.3.6.1 Compressive strength tests

For the strength tests, three cubes were made, wet cured at 23°C and tested for each mix and each age (3, 7, 28 and 90 days) in accordance with SABS Method 863.

4.3.6.2 Chloride conductivity test

The chloride conductivity test was performed in accordance with the standard test method proposed in chapter 7.

4.3.6.3 Oxygen permeability

Results from the permeability test were correlated with in-situ chloride ingress results. These correlations were compared to those of the new chloride conductivity test in chapter 8. A number of researchers focus on permeability as a means of characterising the potential durability of concrete (Ballim, 1991). Oxygen (gas) permeability was chosen for several reasons:

1) Most cements do not react with oxygen.
2) Many substances enter concrete as a gas, ie. CO_2, O_2.
3) The test is of sufficiently short duration to make it useful as an index test.

Ballim's (1991) method was used for the oxygen permeability tests. Concrete specimens, 68 mm diameter and 25 mm thick, are placed in an oven at 50 °C for 7 days to dry. These specimens are then placed in a falling head permeameter. The permeameters are pressurised with oxygen to 100 kPa, and the pressure drop with time to 50 kPa is measured. This data is then used to determine the D'arcy permeability, k (m/s), of the concrete. The negative log of 'k' is taken, and termed the permeability index value. Note that a higher value of k represents a more impermeable concrete.

4.3.6.4 Water Sorptivity

Results from the sorptivity test were correlated with in-situ chloride ingress results. These correlations were compared to that of the new chloride conductivity test in chapter 8.

A modified version (Ballim, 1993) of Kelham's (1988) water sorptivity test was used. Concrete specimens (68 mm diameter and 25 mm thick) are coated with epoxy around their perimeter, and a small reservoir (3 mm deep) is formed by taping insulation tape around the edge. The reservoir is filled with water, and the weight gain of the specimen measured after 1, 2, 4, 8, 16, 32 and 64 minutes. The water in the reservoir is decanted before each weighing, and the reservoir then re-filled. This data is used to calculate the water sorptivity (mm/$\sqrt{}$hr) of the concrete. A lower value of sorptivity represents a better quality concrete.

4.3.7 In-situ tests (Chapter 8)

4.3.7.1 Exposure zone

The concrete blocks were placed in a tidal marine zone in Simonstown (see figure 4.4), and were submerged twice a day. The area is situated inside a small boat harbour, and is sheltered from wave action. The area is exposed to sunlight throughout most of the day. The water temperature varies between 18 °C in summer and 11 °C in winter.

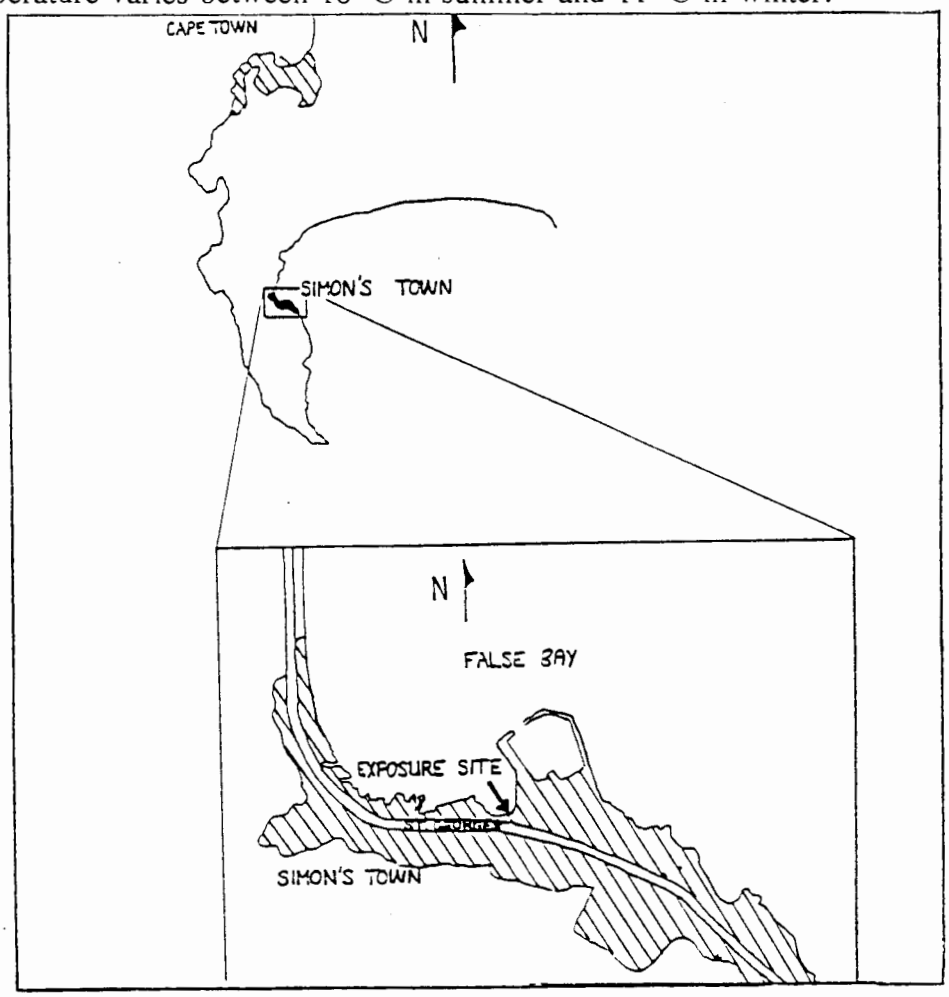

Figure 4.2: Location map.

4.3.7.2 Commencement dates

The concrete blocks were placed in the marine exposure zone in three groups:

1) February 1994 - blocks from mixes 1 - 13

2) August 1994 - blocks from mixes 14 - 24
3) November 1994 - blocks from mixes 25 - 35

4.3.7.3 Drilling procedure and chloride titrations

Drilled powder samples at various depth intervals were obtained after 1 year (+ 0 - 2 months) from one of the two large side faces of all the concrete blocks. Two 20 mm diameter holes were drilled in each block using a Hilti drill. Four depth intervals of 15 mm each were used with the first group. This was changed with the second and third groups since a marked difference in chloride ingress for the different strength grades was observed for the first group. 15 mm intervals were found to be too small for the 20 MPa mixes, and too large for the 60 MPa mixes. The depth intervals used for the second and third groups were:
20 MPa: 20 mm depth intervals
40 MPa: 15 mm depth intervals
60 MPa: 10 mm depth intervals

The acid-soluble chloride contents of the powder samples were obtained using a Mettler Autotitrator. The acid soluble test measures the total chloride content (free and bound chlorides).

4.3.7.4 Acid-soluble chloride test

The acid-soluble test involves adding Nitric acid to the concrete powder to release all the chlorides (bound and unbound). Sodium Acetate is then added to adjust the pH to a suitable level for the Mettler autotitrator (pH 4 - 7). The autotitrator is used with Silver Nitrate as the titrant to determine the amount of chlorides in the powder. A detailed description of the test procedure is given below. It is based on the standard test given in BS 1881 Part 124.

1) Weigh 5 g of concrete powder (fineness $< 150\ \mu m$) in a suitable clean glass flask.
2) Add some distilled water to disperse the powder.
3) Add 2 ml of Nitric acid (diluted 1:1) to the suspension and mix by swirling the flask. Add more distilled water, should the suspension clog together.
4) Leave the suspension to stand for 30 minutes to allow the acid to release all the

chlorides.

5) Add 2.5 ml of Sodium Acetate solution to the suspension to increase the pH to a level of between 4 and 7.

6) Pour the suspension into the plastic cup used in the Mettler titrator. Rinse the solid matter remaining in the flask with distilled water, and pour into the cup. Repeat this three times.

7) Perform the titration by pressing the START button and entering the mass of the powder used (5 g).

8) The titrator will display the percentage chlorides with respect to the concrete powder. This should be converted to a percentage with respect to cement mass based on the original mix design.

The titrator was calibrated from time to time by testing with standard chloride solutions.

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CHAPTER 5

CRITICAL REVIEW OF EXISTING RAPID CHLORIDE TESTS

5.1 INTRODUCTION

The steady state chloride diffusivity of concrete is the most important property governing the time to initiation of reinforcement corrosion in marine environments. Many tests have been developed to determine or estimate the steady state diffusion coefficient of concrete. The tests can be classified into two types:

1. "Classical" steady state diffusion tests which have a sound theoretical basis, but are of too long duration to be of any practical value.
2. Voltage accelerated "rapid chloride tests".

In this chapter existing rapid chloride tests are critically reviewed on the basis of how well the test measures the property under consideration ie. steady state diffusivity (physical resistance of concrete to chloride ingress).

The tests are not criticized on the basis of correlations between test results and chloride ingress on site as this criticism generally relates more to the use of the test results than the test itself. Chloride ingress is a complicated process that involves more factors than just the physical resistance of concrete to chloride transport at a specific time since:-

- concrete properties change with time.
- other mechanisms such as chloride binding, abrasion, water permeation and absorption also play a role.
- the environment will govern to a large degree how these additional factors affect chloride ingress.

5.2 BACKGROUND: RAPID CHLORIDE TESTS

Three types of rapid chloride tests are reviewed in this chapter. It is believed that they represent the range of practical tests presently available. In all three, a concrete specimen is placed adjacent to a chloride solution on the one face, and a chloride-free solution on the other. A potential difference is then applied to draw chloride ions through the concrete.

- The first type of rapid test is represented by the AASHTO T277 or ASTM C1202-91 test, developed by Whiting (1981), in which the total charge passed through a sample during a six hour period under a 60 V potential difference is measured, and the value used as a chloride permeability index. This test is likely to be replaced by an AC impedance test (SHRP-C-361, 1993) or a simple resistivity test (Feldman et al, 1993) which essentially measures the same properties.
- The second type of test is that developed by Dhir et al (1990), who related the steady state chloride flux under a 10 V potential difference empirically to the chloride diffusion D of the concrete.
- The third type of test is represented by the developments of Tang and Nilsson (1992), in whose test the depth of chloride penetration under a 30 V potential after 8 hours is measured, and fundamental electrochemical theory is used to calculate D.

Whiting's (1981) and Tang and Nilsson's (1992) tests are reviewed in this chapter. Dhir et al's (1990) test is dealt with in more detail as it was used extensively in our laboratory and was one of the factors that led to the development of the UCT rapid chloride test.

All the rapid chloride tests are in fact conduction tests. The applied potential difference does not accelerate diffusion, instead it superimposes the mechanism of conduction on diffusion. It can be shown by a simple calculation using equation 3.17 that all rapid chloride tests turn out to be almost pure conduction tests with diffusion playing a very minor role.

Example 5.1 illustrates the voltage required to counterbalance the diffusion flux of chloride ions in a typical rapid chloride test for concrete:

It can be seen that with the voltage accelerated tests, where V is usually very much greater than 0.05 V, predominantly conduction occurs. For example, at a typical value for V of 10 V, J due to conduction would amount to 99.5 % of the total J (assuming steady state conditions).

EXAMPLE 5.1

DATA:

constants:

$$zF = 9.6485 \times 10^4 \ \frac{coul}{mole}$$

$$R = 8.313 \ \frac{J}{K \ mole}$$

assumptions:

$$T = 297 \ K$$

$$c_1 = 1000 \ \frac{mole}{m^3} \quad upstream$$

$$c_2 = 0 \ \frac{mole}{m^3} \quad downstream$$

$$c(ave) = 500 \ \frac{mole}{m^3}$$

SOLUTION:

$$J = \frac{D \ zFE(x)c(x)}{RT} - D \ \frac{dc}{dx} \quad (\ equation\ 3.17\ )$$

$$0 = \frac{D \times 9.65 \times 10^4 \times E \times 500}{8.31 \times 297} - \frac{D \times 1000}{0.04}$$

$$E = 1.28 \ \frac{volts}{m} \quad - \ electric\ field\ required$$

Voltage required for typical 0.04 *m thick sample* = 0.05 *volts*

5.3 WHITING'S (1981) RAPID CHLORIDE PERMEABILITY AND OTHER RELATED TESTS

(RCPT test - ASTM C1202-94; AASHTO T277)

(Proposed AC impedance test; SHRP-C-361 No. 2026)

(Proposed resistivity test; Feldman et al, 1993)

The RCPT test is the most widely used rapid chloride test. The reason is probably the short duration (6 hours) of the test, commercial availability of the test apparatus and the fact that the test has been standardised. The single operator coefficient of variation of the test is

quoted as 12 % and the multilaboratory coefficient of variation of the test is quoted as 18 %. This test will probably be superceded by SHRP-C-361 No. 2026 "Proposed method of test for rapid determination of chloride penetrability of concrete by AC impedance" or by Feldman et al's (1993) resistivity test.

The RCPT test has been used for research studies into the effects of materials and material treatments on chloride resistance, and it has also been used in practice to evaluate concrete materials for new projects that require low chloride permeability, or as a routine quality control measure during construction. In some cases the test has even been used as an acceptance or rejection criterion without correlations with other measures of chloride ion penetrability.

A concrete specimen, 95 mm in diameter and 51 mm thick, is saturated with water under vacuum for 3 hours, and then left to soak in water for 18 hours. The specimen is then placed adjacent to two solutions, one containing 3 % NaCl, and the other containing 0.3 M NaOH. A potential difference of 60 V is applied across the specimen, and the coulombs passed in 6 hours are measured. The value is then used as an chloride permeability index value to rank different concretes (see table 5.1).

Table 5.1: Chloride ion penetrability based on charge passed.

Charge passed (coulombs)	Chloride ion penetrability
> 4000	High
2000 - 4000	Moderate
1000 - 2000	Low
100 - 1000	Very low
< 100	Negligible

Several researchers question the appropriateness of applying coulomb limits to a wide variety of concretes (Pfeifer et al, 1994). They also recommend against using the test results as acceptance or rejection criteria.

The proposed tests by SHRP and Feldman are similar in terms of sample conditioning, but the test procedures involve measuring AC impedance or resistivity of water saturated concrete specimens. An AC impedance measurement at 1000 Hz is similar to a DC (inverse) resistivity (provided polarization is avoided) measurement (Monfore, 1968; Scali et al, 1987; Berke and Roberts, 1989; all in SHRP-C-361). The correlation coefficient, r^2, between the SHRP and RCPT tests is 0.97 (Berke and Roberts, 1989: in SHRP-C-361).

Criticism of the three tests falls into three categories:

5.3.1 Influence of the concrete pore solution conductivity on the test result (all tests)

The critical question that needs to be asked about these tests is whether they accurately measure the permeability of concrete to chloride ions. Unfortunately these tests measure other properties of concrete as well, such as the concrete pore solution conductivity, which are almost irrelevant to the resistance of concrete to chloride ions.

The conductivity, resistivity or impedance of the concrete specimens during these tests depend on two factors (note that any charge flux can only consist of the movement of charged ions through the concrete pore solution) (Atkinson and Nickerson, 1984):

1) The **physical resistance** of the concrete pore structure to ionic flow ie. the constrictivity and tortuosity of the pore passages.
2) The **mobility** and **concentrations** of the various charged ions in the concrete pore solution (pore solution conductivity).

The RCPT test utilises a relatively low concentration chloride solution (3 %) while the SHRP and Feldman's tests involve no chlorides in the specimens. The mobile ions present within the concrete pore solution (K^+, Na^+ and SO_4^{2-}) would therefore contribute significantly to the total charge passed. The concentrations of these ions vary substantially between various cement types. A concrete mix containing silica fume contains much lower concentrations of the mobile alkali ions in the concrete pore solution (Page and Vennesland, 1983) which results in a relatively low RCPT test result compared with other concretes having a similar physical resistance to ionic flow (Streicher and Alexander, 1995). (See later section 6.5.1).

It is for this reason that "conventional concretes made with only portland cement may have coulomb values of 6 - 15 times higher than the same mixture with silica fume cement ... while the actual chloride ingress after 90-day ponding tests may increase only one to two times" (Pfeifer et al, 1994).

5.3.2 Changes in conditions of measurement during the test (only RCPT test)

5.3.2.1 Temperature changes

The temperature of a concrete specimen can rise from room temperature to 100°C during the test. This rise in temperature would vary between different concretes. This is undesirable since most electrochemical processes are temperature dependent (solvation, diffusion, conduction, viscosity). The temperature change might also cause physical and chemical changes to the concrete specimen (Atkinson and Nickerson, 1984).

5.3.2.2 pH changes

During the test, a chloride front will move through the concrete specimen. This will lead to a local decrease in pH as hydroxyl ions are removed to maintain a charge balance (Sergi et al, 1992). A change in pH might cause physical or chemical changes to the concrete specimen.

The conductivity of the concrete pore solution would differ in front of and behind the chloride front, and as this front moves through the concrete, the concrete pore solution conductivity will be changing.

5.3.2.3 Electric potential across specimen

Although a constant 60 V potential difference is applied to the test cells, there will be losses in potential at the electrode/electrolyte interfaces (see section 3.4.3). These losses are variable and depend on a number of factors such as the composition of the electrolyte solution and the quality of the concrete tested. This implies that the actual potential across the concrete specimen would differ from one test to another.

5.3.3 Lack of theoretical basis for tests (all tests)

These tests have no theoretical basis with regard to the parameters involved such as the testing time, specimen thickness, specimen cross-sectional area and voltage applied. The relationships that do exist between the specimen cross-sectional area and the test result are empirical (Mobasher and Mitchell, 1988). Correlations with other long term tests such as the chloride ponding test (AASHTO T259) are also empirical (Pfeifer et al, 1994).

Since there are significant changes in the conditions of measurement during the RCPT test (section 5.3.1.2), it would prove almost impossible to find a theoretical relationship that includes all the test parameters.

The lack of a theoretical relationship for the tests reduce the versatility of the tests; ie. tests can only be performed on concrete specimens with a specified thickness of 51 mm. Also, changing the applied voltage would not necessarily result in similar relative results.

5.3.4 Conclusions

The RCPT, SHRP and Feldman's tests are influenced by the porewater conductivity of the concrete - a factor that is almost irrelevant to the ingress of chloride ions into concrete. There are significant changes in the conditions of measurement during the RCPT test, and the test has no theoretical basis.

Reducing the effect of variable porewater conductivities of different concretes on the test, would involve measuring the chloride flux separately (Dhir et al, 1990; Tang and Nilsson, 1992), or using a high concentration (3 - 5 M) chloride saturating solution (Streicher and Alexander, 1995).

5.4 TANG AND NILSSON'S (1992) RAPID CHLORIDE TEST

The fact that a well defined chloride front moves through the concrete specimen during the initial stages of a conduction test led to the development of this test.

A concrete disc (70 mm thick) is immersed in saturated $Ca(OH)_2$ water for 24 hours and then placed adjacent to a solution containing 3 % NaCl, and one containing $Ca(OH)_2$ saturated water. A potential difference of 30 V is applied across the concrete to pull a chloride front through the concrete. The cell containing the concrete specimen is slanted at an angle, as hydrogen bubbles form on the cathode. After a certain time (8 - 48 hours) the specimen is removed, and the chloride penetration depth determined using a colorimetric method.

Using the Nernst-Planck equation, a relationship between the penetration depth, time of experiment (t) and the diffusion coefficient D was determined:

$$D = \frac{RT}{zFE}\frac{x_f}{t} \qquad (5.2)$$

where x_f ... depth of chloride penetration (m)

5.4.1 Advantages of test

1) The test has a reasonably sound theoretical basis; it includes relevant parameters such as specimen thickness and electric field.
2) The test duration is relatively short.
3) The method of measuring chloride penetration depth requires much less work than continually measuring chloride concentrations.

5.4.2 Disadvantages of test

1) The electric field will differ in front of and behind the chloride front, as well as due to the coarse aggregate distribution, hence it is a function of distance and time, and not a constant as assumed by the authors. This factor will lead to the calculation of lower diffusivities after longer test durations, as was reported by the authors.
2) The test duration required will depend on the quality of the concrete tested. Choosing the incorrect test duration will only be realised after the test.
3) The accuracy of the test depends on how well the chloride front is defined, as well as the distribution of the coarse aggregate (much higher resistivity) in the specimen.
4) As with the ASTM and Dundee rapid chloride tests, the actual voltage across the

concrete specimens will vary from one test to another.

5.5 DUNDEE RAPID CHLORIDE TEST (Dhir et al, 1990)

A modified version of the Dundee rapid chloride test was used for one year in our laboratory. The test was used in the series 1 tests in which a range of condensed silica fume concrete mixes were characterised with respect to marine durability. The experimental details is included in chapter 4. The full set of results is included in Appendix 1 Part B. Experience with the use of this test was a major factor that led to the development of the rapid chloride conduction test.

During trial work with the Dundee test a number of problems were experienced which necessitated some modifications to the test method. Additional modifications were made to simplify the test method, as the project required a large number of specimens to be tested.

Not all the problems experienced could be solved and it was concluded that even with the modifications, the test is not satisfactory.

Observations made in this chapter are explained using the electrochemical principles discussed in chapter 3.

5.5.1 Dundee rapid chloride test (original)

5.5.1.1 Specimens

Concrete or mortar specimens, 100 mm in diameter and 5 - 40 mm thick, are cut from concrete cylinders using a diamond saw. The as-cast surfaces are discarded to reduce variability, and the specimens are lightly ground with silicon carbide paste. The specimens are vacuum saturated with de-ionised water.

A concrete specimen is placed adjacent to two solutions, one containing a 5 M NaCl solution

and the other containing de-ionised water. A potential difference of 10 V is then applied between the anode and cathode. The increase in chloride concentration in the downstream solution is then measured regularly using a chloride ion-selective electrode.

The chloride concentration is plotted against time, and an index (PD) is determined using Fick's First Law when steady state conditions are achieved. It is assumed that the concentration in the chloride solution remains constant.

Dhir et al (1990) conducted pure diffusion tests (D) (0 V potential difference) on the same concretes using the same test arrangement in order to establish a correlation between PD and D. The coefficient of correlation was reported to be good (0.99); however the correlation differed substantially between fly ash and OPC concretes (30 - 70 % difference). The correlation with the pure diffusion test is therefore very dependent on cement composition.

5.5.1.2 Original design of apparatus

The test arrangement differs from conventional two-compartment diffusion tests in that single sided diffusion cells are placed in a large tank containing the chloride solution. This reduces the problem of chloride depletion in the upstream reservoir and makes it possible to conduct multiconcurrent tests.

The tank is constructed of uPVC and insulated with polystyrene. An external plastic impeller pump is used to circulate the solution through a 3 kW heater. Cells of uPVC with a volume of 1 ℓ were chosen to ensure steady state conditions could be maintained for a reasonable period of time.

Graphite anodes, 38 mm in diameter and 100 mm long, are placed in the cells. Graphite was chosen as other metal anodes quickly dissolved, depositing oxides on the specimen surface. A stainless steel plate acting as a cathode is placed at the bottom of the tank.

The potential difference is provided by a 0 - 60 V, 0 - 3 A dc power source, and a chloride ion-selective electrode is used to measure the chloride concentration in the cell solutions.

5.5.2 University of Cape Town (UCT) modified version of the Dundee rapid chloride test

5.5.2.1 Problems with the Dundee test

A number of problems were experienced during trial work with the Dundee test which necessitated some modifications. The problems are discussed along with underlying electrochemical principles involved.

1) Hydrogen generation, acid generation and chlorine evolution

Hydrogen generated at the cathode was trapped under the concrete specimens preventing diffusion of chloride ions. The gas was identified as hydrogen by an ignition test. This resulted in a "popping" sound which is characteristic of hydrogen combustion. The formation of hydrogen is a characteristic cathodic reaction (see section 3.4.3.2).

Acid forming inside the anode cells caused damage to the concrete specimens, and also caused the carbon anodes to dissolve. The pH inside these cells dropped below 1 within a few hours after the potential difference was applied. The consumption of OH^- ions and the generation of H^+ ions are characteristic anodic reactions (see section 3.4.3.2).

Chlorine gas formed in the downstream solution (characteristic unpleasant smell and green colour) which caused a loss of chloride ions. Chloride tests measure the concentration of Cl^- ions in solution, hence chlorine evolution would affect these measurements. Chlorine evolution is a characteristic anodic reaction when chloride ions are present and the solution is acidic (3.4.3.2).

It was found that the addition of an excess $Ca(OH)_2$ on a daily basis kept the anodic solution alkaline and hence prevented damage to the concrete specimens, anodic dissolution and chlorine evolution. This however prevented the use of an ion-selective electrode to measure chloride concentrations in the anodic cells since this method required an acidic solution. To solve this problem it would be necessary to take liquid samples from the anode cells and analyze these separately, however this is a tedious process.

2) Inappropriate test relationship

The relationship used by Dhir to calculate the chloride index proved to be incorrect. Dhir et al (1990) used Fick's First Law (see equation 5.3) to obtain both D and PD. This does not make sense in the case of the rapid test since the application of a potential difference would cause an ionic flux even if the concentration gradient (dc/dx) was zero.

$$J = D \frac{dc}{dx} \quad (\textit{steady state non-voltage test}) \qquad J = PD \frac{dc}{dx} \quad (\textit{voltage accelerated test}) \tag{5.3}$$

Bockris and Reddy (1970) give an equation for the flux of ions under an electric field (see section 3.3.2).

$$J = c\ u\ E \tag{5.4}$$

where c ... ionic concentration (mole/cm^3)
u ... mobility of ions (cm^2/(V.s))
E ... electric field (V/cm)

The electric potential was increased during one trial test, which resulted in a linearly corresponding increase in the measured current. This verified the linear relationship between the ionic flux (J) and the electric field (E).

Clearly, the use of equation 5.4 to obtain a value for PD is incorrect, and the PD value thus obtained can only be regarded as empirical.

3) Potential losses

The test involves applying a constant potential to the cathode and anode. However, potential differences of between 0.5 and 2 V were measured at the electrode-electrolyte interfaces, implying that the potential across the concrete specimens varied between 6 and 9 V. As pointed out in section 3.4.3.2, electron flow is converted to ionic flow at the electrode-electrolyte interfaces by chemical reactions. The reactions result in a potential drop, the

magnitude of which depends on the concentrations of the reagents and reactants present. This factor may influence the repeatability and reproducibility of the test.

5.5.2.2 UCT modified test apparatus

Modifications were made to the original Dundee test apparatus and test procedure to reduce the problems discussed in section 5.5.2.1 and to simplify the test (see figure 5.1). Some of the problems experienced were not resolved as these problems were not fully understood at the time.

A 600 x 600 x 400 mm uninsulated PVC tank (without a heater and external pump) was constructed and placed in a temperature controlled room (25 °C). The solution was circulated with an electric stirrer.

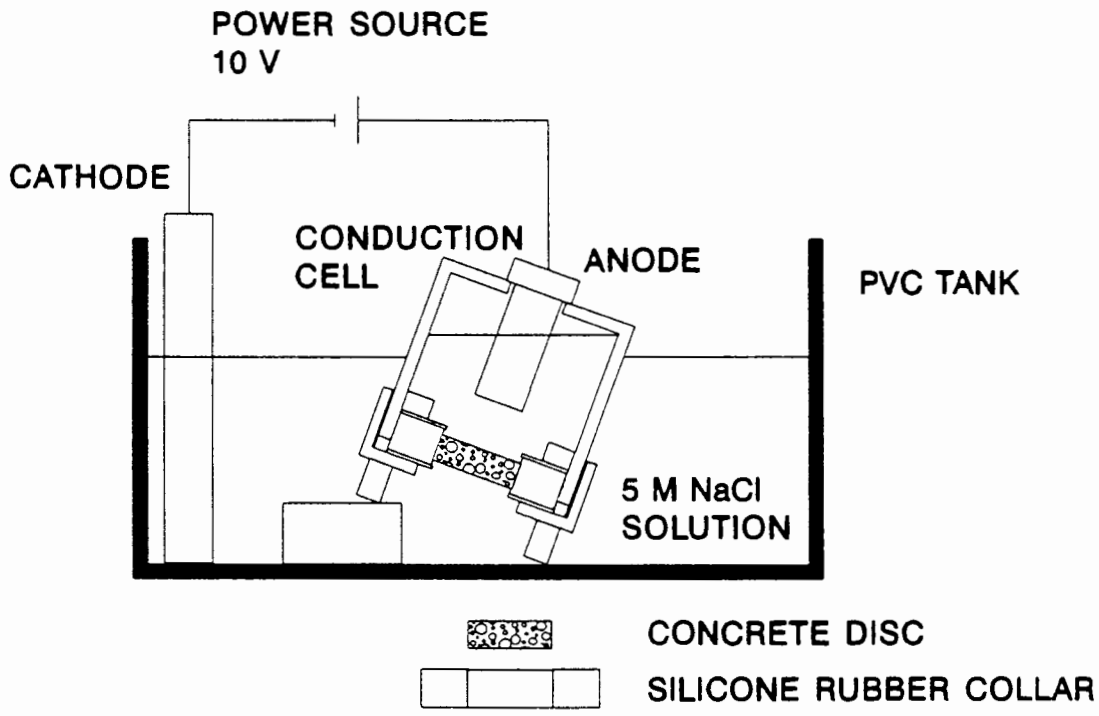

Figure 5.1: UCT modified version of the Dundee rapid chloride test.

The cells were designed for 68 mm diameter concrete specimens of less than 30 mm in thickness. A silicone rubber collar (Shore Hardness = 15) was used to seal the sample into the cell. When the base cover of the cell was screwed on, the sample was clamped by the

lateral Poisson's expansion of the rubber collar.

Grade 316 stainless steel was used for the cathode. The cathode was not placed on the bottom of the tank, but on the side, to prevent hydrogen gas forming on the cathode rising underneath the cells, thus trapping the gas and sealing the specimen from the salt solution. In order to further reduce this problem the cells were also regularly tilted to remove any hydrogen that might have become trapped underneath the cells. This was done before current measurements were taken to ensure that the entire specimen was in contact with the solution at the time. Spacers were also placed underneath the cells so that they stood at an angle to reduce the area of the specimen affected by any trapped hydrogen.

5.5.2.3 UCT modified test procedure

The cells were kept saturated with $Ca(OH)_2$ during the test. This was done to prevent the formation of acid (HCl) and chlorine (Cl_2) and the dissolution of the carbon anodes. This required the addition of $Ca(OH)_2$ on a daily basis.

Instead of measuring the chloride concentration increase in the downstream solution, the total electrical current was measured as an indication of the chloride flux. This was done to simplify the test procedure for the purpose of rapid routine testing. The total electrical current consists of the total ionic charge flux. At this stage, it was assumed that the electric current was predominantly due to the chloride flux due to the high concentration (c) chloride solution used and the high mobility (u) of chloride ions (see equation 3.13)[1]. The remaining portion of the current is carried by other ions such as K^+, Na^+, OH^-, Ca^{2+} and SO_4^{2-}, and although their quantities vary, the effect on the total ionic flux was assumed to be small.

The current measured was used as the result, and was called the "chloride index" value. In retrospect it would have been better to use a parameter such as conductivity which takes account of the applied voltage and the specimen dimensions as well. The specimens tested varied in thickness between 23 and 28 mm. This factor therefore contributed to the variability in results.

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[1] With the development of the new chloride conductivity test, trial work was performed to test this assumption (see chapter 6).

5.5.3 Practical experience with the modified Dundee test

As mentioned, an experimental programme was conducted to assess the chloride penetrability of a range of Portland cement and silica fume blended mixes. The mix variables included different cements, target strengths and initial wet curing periods. The cements comprised an ordinary Portland cement (OPC), blends with undensified condensed silica fume (UCSF) and densified condensed silica fume (DCSF) at different replacement levels. The UCT modified Dundee test was used to characterise the mixes in terms of chloride resistance. A mix was cast and tested (at 28 days) every fortnight. In total, 21 mixes were tested.

A number of concrete cubes cast from the laboratory mixes were placed in sheltered marine spray, tidal and submerged exposure zones. In-situ chloride ingress was measured after two years and correlated with the laboratory test results (see chapter 8).

The focus of this section is on the practical experience with the modified Dundee test.

5.5.3.1 Analysis of typical test observations

Table 5.2 and figure 5.2 shows typical measurements made with the modified Dundee test during the two week testing period. The maximum reading in each case was taken as the chloride index test determination ie. concrete A: 169 mA and concrete B: 81 mA. Three specimens of the same concrete were tested, and the three test determinations were averaged to obtain the chloride index test result.

A number of effects can be observed in figure 5.2:

- The current reduced initially.
- The current then increased until a maximum was reached. There was an inverse relation between the magnitude of the maximum current and the time taken to reach the maximum. Some of the higher strength concretes did not reach a maximum current within the two week period causing some delays.
- After the maximum, the current reduced gradually. The rate of reduction decreased with time.

Table 5.2: Typical measurements made during the test.

Time (days)	Current (mA)	
	Concrete A	Concrete B
0	30	15
1	25	14
2	36	13
3	60	15
4	102	18
5	148	23
6	163	30
7	169	40
8	167	51
9	162	62
10	158	74
11		79
12		81
13		79
14		79

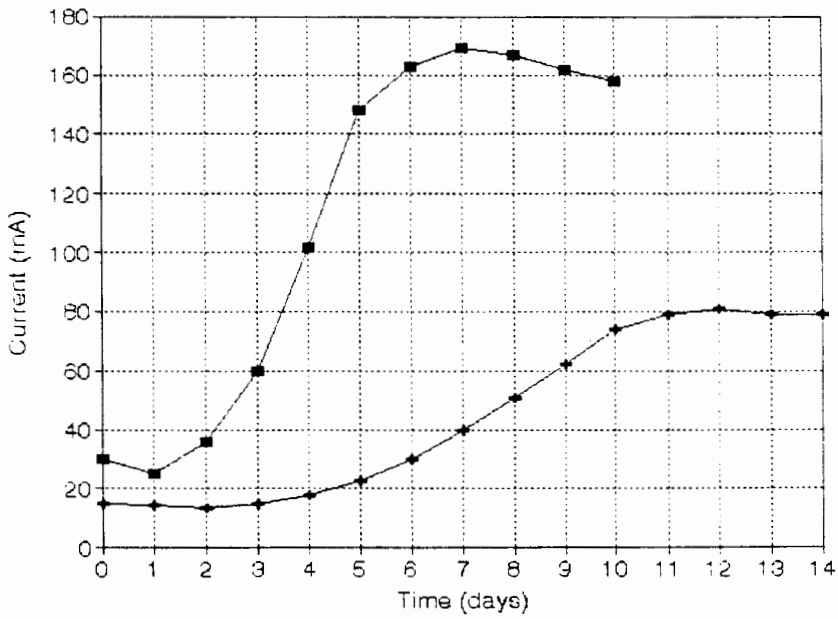

Figure 5.2: Typical measurements made during the test.

The initial reduction in current is probably due to polarisation effects. A constant potential was supplied to the anode and cathode, hence any increase in polarisation resistance at the electrodes will result in a lower current through the specimen.

The increase in current was caused by the movement of a chloride front through the specimen. There is an increase in the electric field in the region ahead of the chloride front (see figure 5.3), because of the lower conductivity of the pore solution (higher resistance) relative to behind the front which contains the high concentration chloride solution. When the maximum current is reached, the chloride front has moved through the sample, and the chloride concentration within the sample has reached equilibrium conditions ie. constant concentration throughout the specimen.

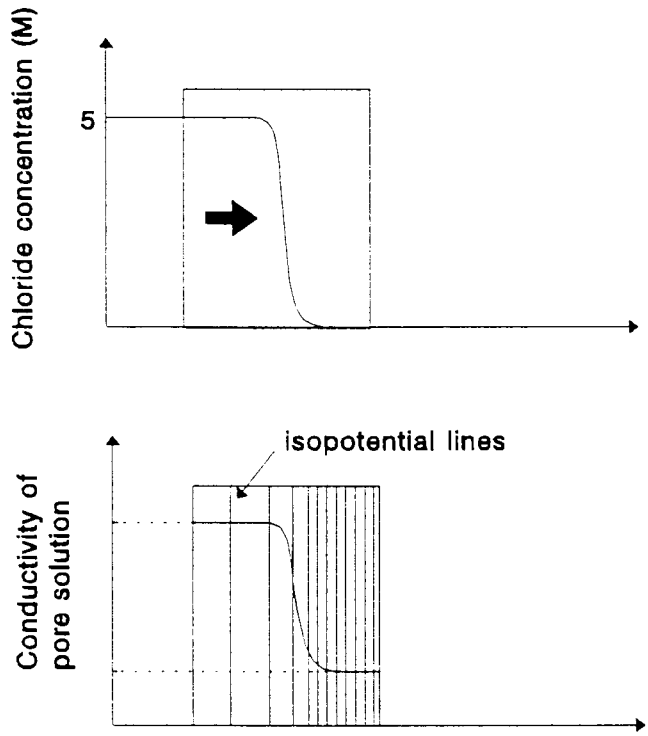

Figure 5.3: Increase in electric field ahead of chloride front.

With an inert porous material, the current would have reached a constant level at this stage (steady state conditions). However, with the concretes tested, a reduction in current was observed indicating an increase in resistance of the specimens to chloride transport. The condition where a constant chloride profile is reached was therefore defined as the "quasi-steady state" condition. Quasi-steady state conditions are reached when the current reaches a maximum.

The pore structure of concrete is refined by hydration which could contribute to explain the reduction in current. Concrete also reacts with chloride ions (chloride binding). It was speculated that the reaction products of this reaction might constrict the concrete pores increasing the resistance of the concrete to chloride transport. This process is time-dependent, which means that the degree of interactions measured would vary as the testing times vary. This process is discussed in more detail in section 5.5.

5.5.3.2 Typical test results

Figures 5.4 and 5.5 show typical test results using the modified Dundee test. From the results it can be seen that the test is sufficiently sensitive to the measured property in terms of changes in strength grade, curing regime and cement type.

The single-operator coefficient of variation of the modified Dundee test was estimated to be 12 % using the method described in chapter 7.

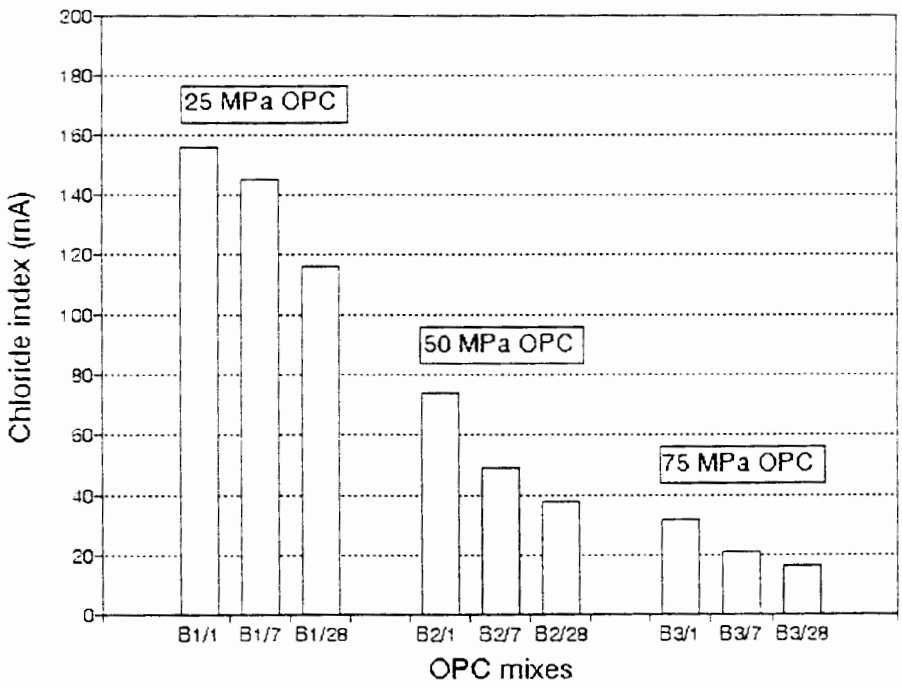

Figure 5.4: Chloride index results: OPC mixes. B1/1 refers to the mix number and B1/1 refers to the wet curing time in days.

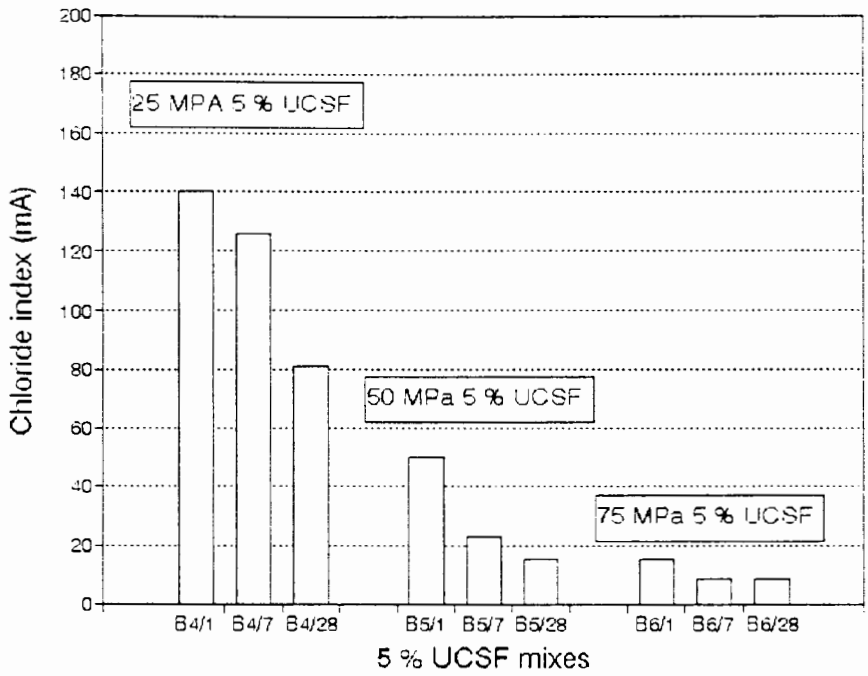

Figure 5.5: Chloride index results: 5 % UCSF mixes.

5.5.3.3 Additional modifications

The test could be further improved by using conductivity (σ) as the test parameter instead of electric current. This parameter will take account of the potential applied and the specimen dimensions. The use of Luggin capillaries are suggested to more accurately measure the applied potential across the specimen (see Chapter 6).

5.5.4 Reduction in conductivity with time

The mathematical model of Dhir et al's (1990) test implies that after steady state conditions have been reached, the chloride flux ($\approx$ ionic flux (electric current)) through the concrete specimen will be constant. However, during the tests performed, the current measured increased up to a point and then decreased again (see figure 5.2). The rate of decrease was found to be very dependent on cement composition (Streicher et al, 1994).

When an electric potential difference is applied at the start of the test, a chloride front is pulled through the concrete specimen (Tang and Nilsson, 1992). Quasi-steady state conditions

are reached when the front has passed through the concrete. The chloride concentration in the pore water is then constant, and equal to that of the source solution. Although the physical and chemical binding of ions would deplete some of the chloride ions, the constant flux of ions would replace these ions keeping the conductivity of the pore solution constant. A drop in the steady state current would therefore indicate an increase in the physical resistance of the concrete to ionic transport ie. an increase in the tortuosity and constrictivity of the pores (Atkinson and Nickerson, 1984).

Although additional hydration would reduce the steady state current, the decrease in current far exceeded the rate expected were additional hydration the only factor. It is believed that the reduction in steady state current was also caused by changes in the physical pore structure of the concrete due to chemical interactions between chloride ions and the cement. The use of a very high concentration (5 M) chloride solution increase the likelihood of this theory. This issue is dealt with in detail in chapter 6.

A certain degree of the chemical changes observed after the maximum current was reached must have occurred before the maximum current was reached. For concretes with low conductivities (longer testing times) it is likely that a greater degree of chemical changes occurred before this point relative to concretes with higher conductivities (shorter testing times). With the Dundee test it is not possible to avoid these changes. There is therefore a potential discrepancy in the property measured.

5.6 CONCLUSIONS

The RCPT, SHRP and Feldman tests have a number of serious problems associated with them, the most important being that these tests are severely influenced by the porewater conductivity of the concrete which is irrelevant to the physical resistance of concrete to chloride ingress. These tests are therefore not suitable for characterising the physical resistance of concrete to chloride ingress.

Tang and Nilsson's (1992) rapid chloride test appears more suitable, on the basis of simplicity, theoretical basis and versatility. Practical experience is however necessary to

determine the precision of the test.

The Dundee test had a number of problems which necessitated modifications to the test procedure. The modifications are summarised below:

1) Calcium hydroxide is added to the anode solution to prevent acid formation, chlorine evolution and the dissolution of the carbon anode.
2) The cells are tilted and the cathode placed on the side of the tank to reduce the problem of hydrogen trapped under the cells (which reduce the wetted surface area of the specimens).
3) The electric current is measured instead of chloride flux to make the test more suitable for rapid routine testing.

The test was used in an experimental programme to study the marine durability properties of condensed silica fume mixes. The test was found to be sensitive to the variables tested ie. cement type, curing and target strength.

Additional modifications were suggested:

1) The use of conductivity (σ) as the test parameter to take account of the test variables: applied voltage and specimen dimensions.
2) The use of Luggin capillaries to accurately measure the applied voltage across the specimen.

Even with the modifications the test is still of too long duration for rapid routine testing (2 weeks).

A reduction in electric current was measured after the quasi-steady state conditions were achieved, indicating possible chemical interactions between the concrete and the high concentration chloride solution. There is uncertainty as to what degree these chemical changes affect the test results.

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CHAPTER 6

DEVELOPMENT OF THE CHLORIDE CONDUCTION TEST

6.1 INTRODUCTION

Rapid chloride tests have been used to compare the resistance of different concretes to chloride ingress. This has proved very useful in finding economical mixes for high durability applications, and has also helped in understanding the factors that improve the resistance of concrete to chloride ingress.

Three types of rapid chloride tests have been developed to date. In all three, a concrete specimen is placed adjacent to a chloride solution on the one face, and a chloride-free solution on the other. A potential difference is then applied to draw chloride ions through the concrete. The first type of rapid test is represented by the AASHTO T277 test, developed by Whiting (1981), in which the total charge passed through a specimen during a six hour period under a 60 V potential difference is measured, and the value used as a chloride permeability index. The second type of test is that developed by Dhir et al (1990), who related the steady state chloride flux under a 10 V potential difference empirically to the chloride diffusion D of the concrete. The third type of test is represented by the developments of Tang and Nilsson (1992), in whose test the depth of chloride penetration under a 30 V potential after 8 hours is measured, and fundamental electrochemical theory is used to calculate D.

The electric potential does not accelerate the mechanism of diffusion. The increased flux of ions is caused almost solely by the mechanism of conduction (chapter 5). Since these tests increase the ionic flux up to a 100 times, they are essentially conduction tests with negligible diffusion. Feldman et al (1993) have shown that a simple conduction test on "virgin" concrete gives the same ranking as Whiting's (1981) test and proposed the replacement of AASHTO T277 with a resistivity (conductivity) test.

Both Whiting's test and the proposed resistivity test of Feldman et al are influenced by the variability of the pore water conductivity of various concretes (see chapter 5). This variability results in the index obtained not necessarily being proportional to the steady state diffusion coefficient. Cement types such as silica fume blends give very low pore water conductivities.

Using these tests to evaluate the relative performance of different cement blends would therefore be doubtful. Although the test of Dhir et al and Tang and Nilsson obviate this problem, the AASHTO test is still the most widely used because it is so rapid.

There is therefore a need for a chloride test that is theoretically sound, and that is as rapid or more rapid than the AASHTO test.

This chapter describes the development of the rapid chloride conduction test. The test is virtually independent of the concrete pore solution conductivity. The electrochemical principles that led to the development of the test and the trial tests used to optimise and verify the test procedure are discussed.

6.2 OBJECTIVES FOR NEW CHLORIDE TEST

The objective was to develop a chloride test which:

- estimates the steady state diffusivity (physical resistance to chloride ingress) of concrete accurately and has a sound theoretical basis.
- is rapid, efficient and simple to perform.
- is sensitive to the measured property in terms of important material and environmental factors.
- is repeatable and reproducible.
- is of low cost.

6.3 DEVELOPMENT OF THE UCT RAPID CHLORIDE CONDUCTION TEST

The development of the new chloride test was based on the ionic distribution that pertains during steady state conduction. Diffusivity and conductivity are most easily measured and calculated under steady state conditions. With pure diffusion tests, a period of a year or more is needed before steady state conditions are achieved in concrete specimens of suitable thickness. With Dhir et al's (1990) conduction test, steady state conditions are achieved after about 7 days. The fact is not always appreciated that the ionic distribution during steady state

conditions differs for the two types of test.

The ionic concentration gradient is the driving force behind diffusion, and a steeper gradient increases the rate of diffusion. With steady state diffusion the concentration gradient has a constant slope (see figure 6.1).

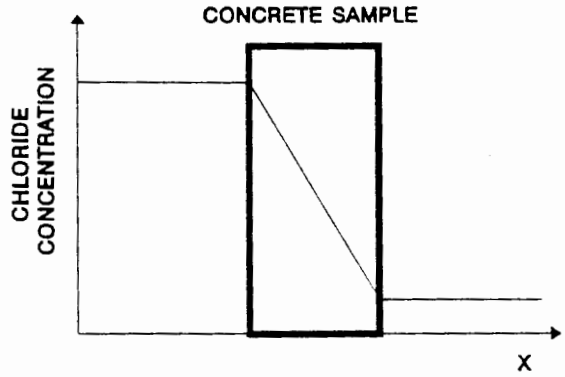

Figure 6.1: Steady state diffusion.

With conduction the driving force is the electric field. In the same electric field each charge would experience the same force. Thus, in steady state conduction the electric field is constant, and the charged ions are uniformly distributed (see figure 6.2).

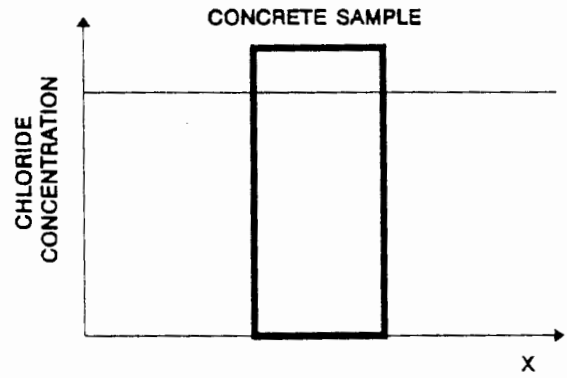

Figure 6.2: Steady state conduction.

At the start of a conduction test the chloride ions move through the concrete in a well defined front (Tang and Nilsson, 1992). Steady state conditions are achieved when the front has passed through the concrete sample. The chloride concentration in the pore solution of the concrete is then uniform (see figure 6.3). This can be exploited to permit a very rapid chloride test, since virtually the same condition can be achieved in a much shorter time by vacuum-saturating a concrete sample with a chloride solution.

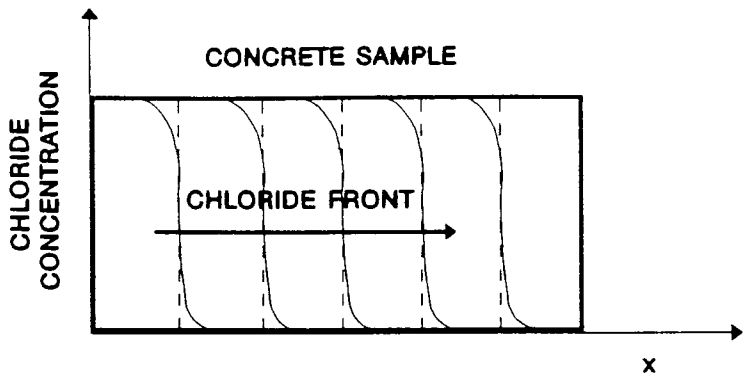

Figure 6.3: Chloride front during conduction tests.

With Dhir et al's test (1990) the condition required for steady state conduction is achieved after several days by electrically pulling a chloride front through a water saturated concrete. By initially saturating the samples in a chloride solution steady state conditions pertain from the start (see figure 6.4).

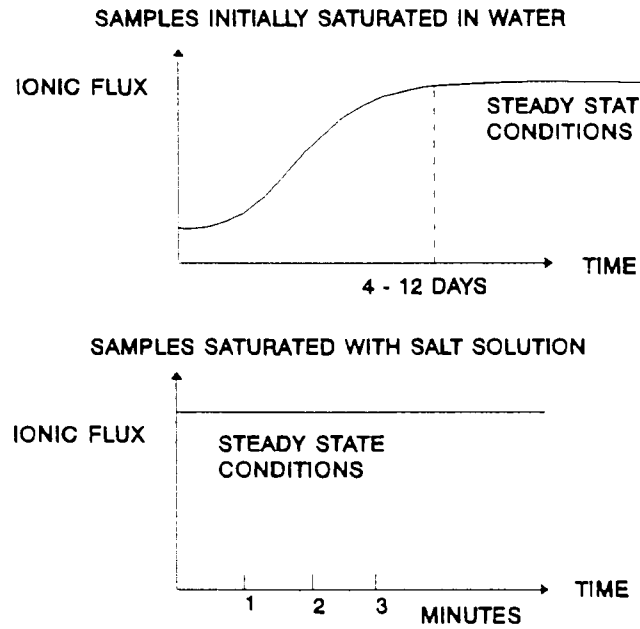

Figure 6.4: The effect of saturating with a salt solution.

To avoid dilution of the chloride solution inside the concrete, the specimens require drying prior to immersion. The test is further simplified by measuring the electric current instead of measuring the chloride flux. The current measurement is readily converted into a conductivity value.

In essence, the test therefore involves:

- Sample preparation - coring / cutting
- Sample conditioning - drying / saturation
- Placing of sample in apparatus
- Take instantaneous reading of current under applied voltage

6.4 RELATIONSHIPS BETWEEN DIFFUSIVITY AND CONDUCTIVITY

Although diffusion and conduction are different transport mechanisms, at low concentrations both are linearly related by Einstein's relationship (eq. 3.16):

$$u = zF \frac{D}{RT} \tag{6.1}$$

where u ... mobility of ion
z ... charge of ion
F ... Faraday's constant
D ... diffusivity of ion
R ... gas constant
T ... absolute temperature

At higher concentrations there are various factors that influence each mechanism differently. Another relationship involving both diffusion and conduction parameters, the Nernst-Planck equation (eq. 3.17), is derived from Einstein's relationship and also apply only under ideal conditions (Bockris and Ready, 1970).

In a porous medium the rate of each mechanism would be affected by the tortuosity and constrictivity of the pore structure (Atkinson and Nickerson, 1984). A material constant Q (diffusibility) is defined in equation 6.2 as the ratio between the diffusivity of an ion in a porous material to that of the same ion in the pore solution only. This constant is also equal to the ratio between the mobility (or conductivity) of an ion in a porous medium to that of the same ion in the pore solution (Garboczi and Bentz, 1992). (Note that both the diffusivity and mobility coefficients in the porous material are in terms of the average flux per unit area of the medium.)

$$Q = \frac{D_s}{D_f} = \frac{\sigma_s}{\sigma_f} \qquad (6.2)$$

where Q ... diffusibility of porous medium
D_s ... diffusivity of ion through porous material
D_f ... diffusivity of ion through pore solution
σ_s ... conductivity of porous medium
σ_f ... conductivity of pore solution

Note that this relationship applies for both low and high concentration solutions since the non-ideal factors in the numerator and demoninator cancel each other.

Theoretically it is therefore possible to determine the chloride diffusivity of a porous medium by conductivity measurements. By measuring the conductivity of the porous medium, and the conductivity of its pore fluid, the diffusibility ratio is obtained. This number is then multiplied by the diffusivity of chloride ions in the pore solution to obtain the chloride diffusivity of the porous medium.

Although the diffusivity of concrete has been determined from conductivity measurements using the Nernst-Planck electrochemical relationship, the non-ideal nature of the solutions used affect this relationship. Andrade's (1993) method of calculating D also requires the transport number of the chloride ions, ie. what percentage they are contributing to the current. This number varies, and to determine the chloride flux alone would be time consuming. Using the diffusibility ratio eliminates these problems, since both solutions contain the same ions at the same concentrations ie. they have the same chloride transport numbers and the same activity coefficients.

This method is also suited to the proposed conductivity test since the conductivity of the pore solution (σ_0) can be shown to be very little different from that of the 5 M NaCl saturating solution (see section 6.6.1).

6.5 PRELIMINARY DESIGN OF TEST APPARATUS AND PRELIMINARY TEST METHOD

The objective was to design a testing apparatus that performs a rapid, accurate and inexpensive measurement of the dc conductivity of a concrete specimen (5 M NaCl saturated), independent of outside influences and polarisation effects.

Determining the conductivity of the concrete specimen would involve four measurements: the thickness of the specimen, the cross-sectional area of the specimen, the electric current flowing through the specimen and the potential difference across the specimen.

The characteristics of the new test determined the design of the test apparatus. Since the test involves a single current and voltage reading, the apparatus can be used consecutively on a series of specimens. The time taken to set up the apparatus for each test determines the rate at which samples can be tested. During the short duration of the test (< 30 s) relatively few ions migrate and small cells can therefore be used.

6.5.1 Cells and silicone rubber collar

The conduction test apparatus was designed with two 500 ml cells adjacent to a central section containing the concrete specimen (see figure 6.5). Both cells were designed to screw onto the central section, thus compressing the silicone rubber collar and clamping the specimen (Poisson's effect). Each cell was to contain a 5 M NaCl solution. By holding the apparatus in either vertical position each cell could then be removed without spilling the cell solution.

6.5.2 Anode, cathode and power source

A carbon anode and a stainless steel cathode were chosen as these were used successfully with the Dundee test in our laboratory. Dhir et al (1990) reported that metal anodes dissolved, depositing metal oxides on the specimen surfaces. A 0 - 20 V (0 - 3 A) dc power source was purchased to apply the potential difference (see figure 6.5).

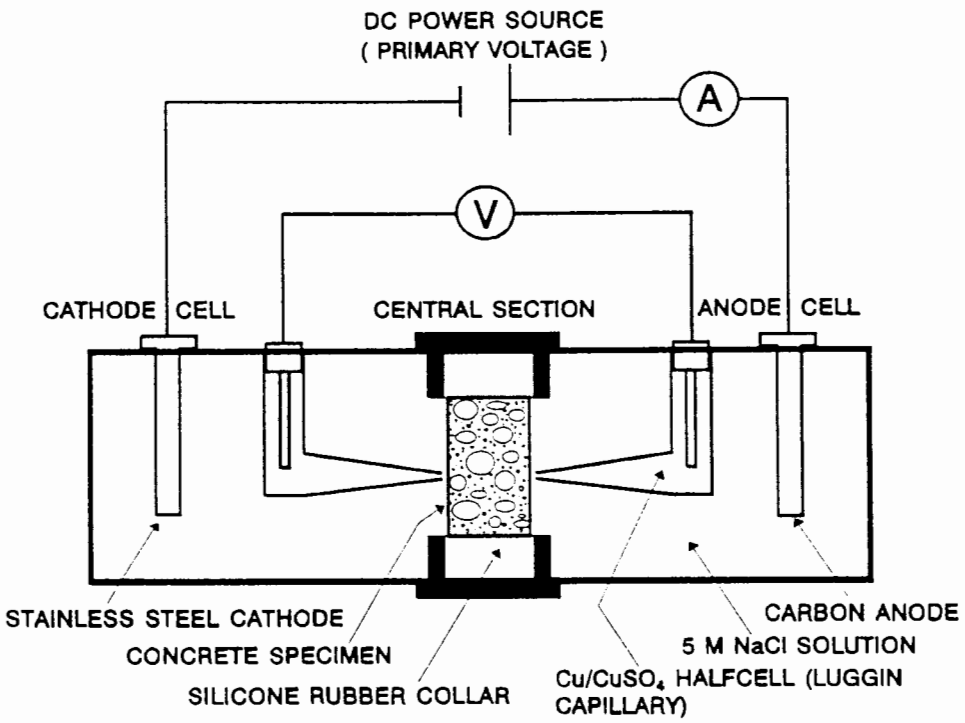

Figure 6.5: Schematic representation of the conduction test arrangement.

6.5.3 Halfcells and Luggin capillaries (Electric potential measurements)

The potential difference across the specimen is the most difficult measurement to make, since it involves measuring the potential between two electrolyte solutions adjacent to both sides of the concrete specimen.

An electrolyte-saturated concrete specimen will conduct an electrical current by ionic migration through the pore fluid. The solid pore structure can be assumed to be non-conductive as it consists of covalently bonded elements and has a conductivity 400 times lower than that of the pore fluid (Atkinson and Nickerson, 1984).

As shown in figure 3.3, there are potential losses in the connecting wires, at the electrode/electrolyte interfaces and in the solutions adjacent to the sample. These potential losses could vary depending on the length of the wires, the size and type of electrodes and the size of the cells and concentration of the cell solutions used.

With other rapid chloride tests two cells containing different solutions are placed adjacent to

the concrete specimen and the electric potential is applied through an anode and cathode immersed in the each solution. With most of these tests, the electric potential is measured at the power source (AASHTO test (Whiting, 1981), Dundee test (Dhir, 1991), Tang and Nillson's (1992) test).

If these tests are to be used in different laboratories, very strict specifications will be needed on all the design aspects and operating procedures of the apparatus and the test (since all these factors could influence the magnitude of the potential losses).

The UCT chloride conduction test apparatus was designed with two standard copper/copper sulphate halfcells, each including plastic tubes (Luggin capillaries) leading to both sides of the specimen (see figure 6.5). This was done to ensure the accurate measurement of the potential difference between the solutions adjacent to the specimen surfaces. With normal voltmeter electrodes, the measurements would have been influenced by the electrode material, size of the electrode as well as the electrolyte solutions surrounding the electrodes. With standard halfcells, the electrolyte solution and electrode material and size are specified. The electrolyte solution in the Luggin capillaries would include the same metal ions as that of the electrode to prevent unwanted deposits on the electrode.

6.5.4 Voltmeter and ammeter

A voltmeter that could measure a dc voltage between 0 and 20 V to an accuracy of $\pm$ 0.05 V, and an ammeter that could measure a dc current between 0 - 300 mA to an accuracy of $\pm$ 1 mA was chosen based on experience with the Dundee test.

The voltmeter was to be connected in parallel with the cell, and the ammeter was to be connected in series with both (see figure 6.5) so that the ammeter measures both the current through the cell and the voltmeter. Although voltmeters do allow some current through, the range of resistance of different concrete specimens was generally found (with the Dundee test) to be much lower compared to that of the voltmeter ie. the current through the voltmeter can be assumed to be negligible.

6.5.5 Sample conditioning

Sample conditioning for the chloride conduction test consists of drying the concrete specimens and then saturating them with a 5 M NaCl solution.

The objective of the drying procedure was to dry the concrete specimens sufficiently without causing undue damage in terms of the measured property. By "sufficient drying" is meant that the moisture remaining in the concrete should not dilute the saturating solution significantly (in terms of the measured property), or prevent the saturating solution from reaching all the pores.

The drying procedure needed to be practical for routine rapid testing including site use. Oven drying was regarded as the only practical method.

The objective of the saturating procedure was to saturate the concrete specimens such that the entire pore volume practically has the conductivity of the saturating solution.

A vacuum saturating procedure was chosen to minimise the saturation time required. An Edwards vacuum pump was used for the saturation procedure. A PVC cylinder which could withstand vacuum pressures was designed to house the specimens, and a 45 L pressure vessel was purchased to act as a water trap between the pump and the cylinder.

6.5.6 Saturating solution

A 5 M NaCl solution was chosen to saturate the concrete.

$CaCl_2$ was initially considered as calcium ions have a very low mobility compared to chloride ions (Ca/Cl mobility = 0.01) and would not contribute to the ionic flux in the conduction test. The mobility of sodium ions is similar to that of chloride ions (Na/Cl mobility = 0.656), and would therefore contribute to 39.6 % of the total ionic flux. However, the low solubility of $Ca(OH)_2$ might cause substantial precipitation of calcium in the form of $Ca(OH)_2$, blocking the pore space leaving mainly Cl^-, K^+ and Na^+ ions in solution. Sodium chloride was therefore chosen.

The high concentration (5 M) solution was used successfully with the Dundee test. The advantage of using a high concentration solution is that it is likely to reduce interferences from other ions present in the concrete pores. It is also likely to reduce the effect of dilution (due to chloride binding) on the conductivity of the solution. These aspects are further dealt with later.

6.6 VERIFICATION OF THE CHLORIDE CONDUCTIVITY TEST

The following aspects of the test were verified:

6.6.1 Conductivity of the concrete pore solution.

6.6.2 Sample conditioning - oven drying.

6.6.3 Thickness tests: Conductivity relationship
Saturating procedure
Representative concrete specimen sizes.

6.6.1 Conductivity of the concrete pore solution

Saturating the concrete specimens with a highly conductive solution in the chloride conduction test is aimed at ensuring that all specimens have practically the same pore solution conductivity. This section deals with the verification of this assumption.

The porewater conductivity of concrete is very dependent on the cement composition. Page and Vennesland (1983) measured the ionic concentrations in the porewater of an ordinary portland cement (OPC) paste and a cement silica fume blend paste (see table 6.1). The cement used had relatively high Na_2O and K_2O contents of 0.41 % and 1.18 % respectively.

Table 6.1: Porewater compositions of OPC and silica fume pastes at 28 days (Page and Vennesland, 1983).

@ 28 days	K^+	Na^+	OH^-	SO_4^{2-}
OPC	0.63 M	0.27 M	0.83 M	0.31 M
OPC, 20 % SF	0.11 M	0.06 M	0.09 M	0.33 M

The equivalent conductivities (see Chapter 3, table 3.6) of K^+, Na^+ and OH^- are 75, 50 and 200 S/(cm^{2}mole). The pore solution conductivity of the OPC paste would therefore be approximately 7 times higher than that of the silica fume paste (using equation 3.13).

The conductivities of different saturated concretes would therefore not be directly proportional to their diffusibilities (see equation 6.2).

The conductivity of the saturating salt solution can easily be measured. However, mobile ions such as K^+, Na^+ and OH^- are also present in concrete pores, and these ions would affect the conductivity of the pore solution (σ_o) to a certain degree. Artificial solutions were used to determine to what degree typical alkali metal concentrations would affect the pore solution conductivity.

The conductivities of NaCl solutions of different concentrations were determined theoretically and experimentally. Similar solutions, but also containing KOH and $Ca(OH)_2$, were also tested to determine what effect these ions have on the conductivity of NaCl solutions.

The conductivities of nominally identical mortar samples (cored from the same specimen) saturated with NaCl solutions of various concentrations were determined using the conductivity test. The diffusibility ratio (Q) was calculated for two different assumed values of σ_o. This was done to demonstrate the sensitivity of Q to σ_o using different concentration chloride solutions.

6.6.1.1 Conductivities of concentrated solutions

Robinson and Stokes (1955) give a general, approximate equation for the conductivity of a concentrated 1:1 electrolyte (eg. LiCl, NaCl, KCl etc.) (equation 6.3). This equation is empirical, and takes into account all non-ideal effects. Viscosity increases rapidly with higher concentrations for some electrolytes, hence a term for the relative viscosity of the electrolyte is included.

$$\Lambda = \frac{\eta_0}{\eta}\left(\Lambda_0 - \frac{B_2\sqrt{c}}{1+B\mathring{a}\sqrt{c}}\right)\left(1 - \frac{B_1\sqrt{c}\,f}{1+B\mathring{a}\sqrt{c}}\right) \qquad (6.3)$$

where Λ ... molar conductivity of solution [Scm^2/mole]

Λ_0 ... equivalent conductivity, 0 concentration [Scm^2/mole]

η_0/η ... relative viscosity of solution

B, B_1, B_2 ... temperature dependent constants (see table 6.2)

c ... ionic concentration [mole/l]

å ... ionic radius [Å]

f ... factor (see equation 6.4)

$$f = \frac{e^{0.2929\kappa\alpha} - 1}{0.2929\kappa\alpha} \quad where \quad \kappa\alpha = B\mathring{a}\sqrt{c} \qquad (6.4)$$

Robinson and Stokes (1955) compared the predictions of equation 6.3 with observed conductivities for LiCl up to a concentration of 9 M. The maximum difference between the two was about 5 %. Although the comparison is approximate, it is still very useful.

6.6.1.2 Calculation of conductivities of 0 - 5 M NaCl solutions at 25 °C

Equation 6.3 was used to calculate the conductivities of NaCl solutions for concentrations 0 to 5 M at 25 °C:

For NaCl: å = 4.0 Å, Λ_0 = 126.45 Scm^2/mole (25 °C) - Robinson and Stokes (1955).

At 25 °C: B_1 = 0.2289, B_2 = 60.32, B = 0.3286 - table 6.2.

f is given in table 6.3 ($\kappa\alpha = 1.3144\sqrt{c}$).

Table 6.2: Temperature dependant constants for use in equation 6.3.

Temperature (°C)	B_1	B_2	B
10	0.2231	40.86	0.3258
15	0.2249	47.01	0.3267
20	0.2269	53.48	0.3276
25	0.2289	60.32	0.3286
30	0.2311	67.54	0.3297

Table 6.3: Values of factor f (25 °C).

c [M]	F
0.5	1.150
1.0	1.221
1.5	1.279
2.0	1.331
3.0	1.427
4.0	1.512
5.0	1.587

The relative viscosities of the various solutions were calculated using Bingham's (1941) method. He showed that the change in fluidity (reciprocal of viscosity) of a solution is equal to the sum of the change in fluidity caused by the cations and the change in fluidity caused by the anions. The change in fluidity per unit concentration for Na^+ is -9.6 rhes and for Cl^- it is 0.28 rhes. The relative viscosities calculated were verified using an Ubeholde viscometer in our laboratory. The calculated and observed values are displayed in table 6.4.

Table 6.4: Relative viscosities of NaCl solutions (Bingham, 1941).

Concentration NaCl [M]	Δm (change in fluidity of medium) $= c(\Delta c + \Delta a)$	ϕ (fluidity of medium) $= \phi_w + \Delta m$ (ϕ_w = 111.91 rhes)	η_w/η (relative viscosity) $= \phi/\phi_w$	η_w/η (measured with Ubeholde viscometer)
0.5	-4.66	107.24	0.958	-
1.0	-9.32	102.6	0.917	0.93
1.5	-13.98	97.93	0.875	0.87
2.0	-18.64	93.27	0.833	0.83
3.0	-27.96	83.95	0.750	0.74
4.0	-37.28	74.63	0.667	0.64
5.0	-46.60	65.31	0.584	0.59

Table 6.5 shows the solutions to equation 6.3. The values calculated for the various terms are also shown.

Table 6.5: Solutions to equation 6.3.

Concentr. NaCl [M]	Relative viscosity	Term 1	Term 2	Molar conduct. (Scm^2mole^{-1})	Conduct. (mS/cm)
		Equation 6.3			
0.5	0.958	104.34	0.9035	90.12	45.16
1.0	0.917	100.39	0.8792	80.67	80.67
1.5	0.875	98.14	0.8626	73.99	111.1
2.0	0.833	96.61	0.8493	68.59	136.7
3.0	0.750	94.56	0.8273	59.77	176.0
4.0	0.667	93.20	0.8093	52.65	201.2
5.0	0.584	92.21	0.7938	46.70	213.7

6.6.1.3 Measured conductivities of NaCl solutions at various concentrations (25 °C).

The conductivities of 0.5, 1, 1.5 and 2 M NaCl solutions were measured with a conductivity meter (HANNA Instruments HI 8820). Similar solutions, but containing KOH and $Ca(OH)_2$, were also tested to determine what effect these ions have on the conductivity of NaCl solutions. Two levels of KOH (0.16 and 0.32 M) were added to similar sets of NaCl solutions. The levels were chosen to achieve pH levels of 12.5 (no KOH), 13.2 and 13.5 which are typical levels found in concrete pore solutions (Moragues et al, 1987).

Measurements showed that the addition of $Ca(OH)_2$ (low solubility) did not alter the conductivity of the KOH solutions; ie. the conductivity or resistivity of water-saturated concrete is governed by the level of alkali metal ions.

The meter was calibrated with a 80 mS/cm buffer solution, and had an accuracy of 0.2 mS/cm in the range 0 - 99.9 mS/cm. The maximum displayed reading was 199.9 mS/cm. Higher concentration solutions (3, 4 and 5 M) were not tested as these fell outside the range of the meter. The meter contains a thermometer and converts the readings to a conductivity at 25 °C. The temperature compensation coefficient β was set at 1.5 %. The measured values are displayed in table 6.6.

The measured results of all the solutions were plotted on a graph (see figure 6.6). The values calculated for NaCl were plotted as a curve (the lower one).

The addition of KOH caused an increase in conductivity which reduced with the increase in NaCl concentration, attributed to the increase in viscosity of the NaCl solutions. It can be assumed that the addition of KOH did not alter the viscosity of the solution due to the relatively low quantity added. Curves were fitted to the measured points on this basis (see equation 6.5) in figure 6.6 (upper 2 curves).

$$\sigma_{sol} = \sigma_{NaCl} + \frac{\eta_o}{\eta_{NaCl}} \sigma_{KOH} \qquad (6.5)$$

where σ_{sol} ... conductivity of composite solution (see figure 6.6)

σ_{NaCl} ... calculated conductivity of NaCl solution

$\eta_0/\eta_{NaCl}\ \sigma_{KOH}$ ... increase in conductivity after KOH addition

Table 6.6: Measured conductivities for solutions containing KOH additions.

Concentration NaCl [M]	Conductivity measured (NaCl only) (mS/cm)	Conductivity measured (0.16 M KOH, $Ca(OH)_2$ sat) (mS/cm)	Conductivity measured (0.32 M KOH, $Ca(OH)_2$ sat) (mS/cm)	Increase in conductivity (mS/cm) col.
0	0	36	63	63
0.5	45	78	102	57
1.0	81	111	134	53
1.5	110	139	161	51
2.0	139	165		
2.5	162	-- exceeded	range --	

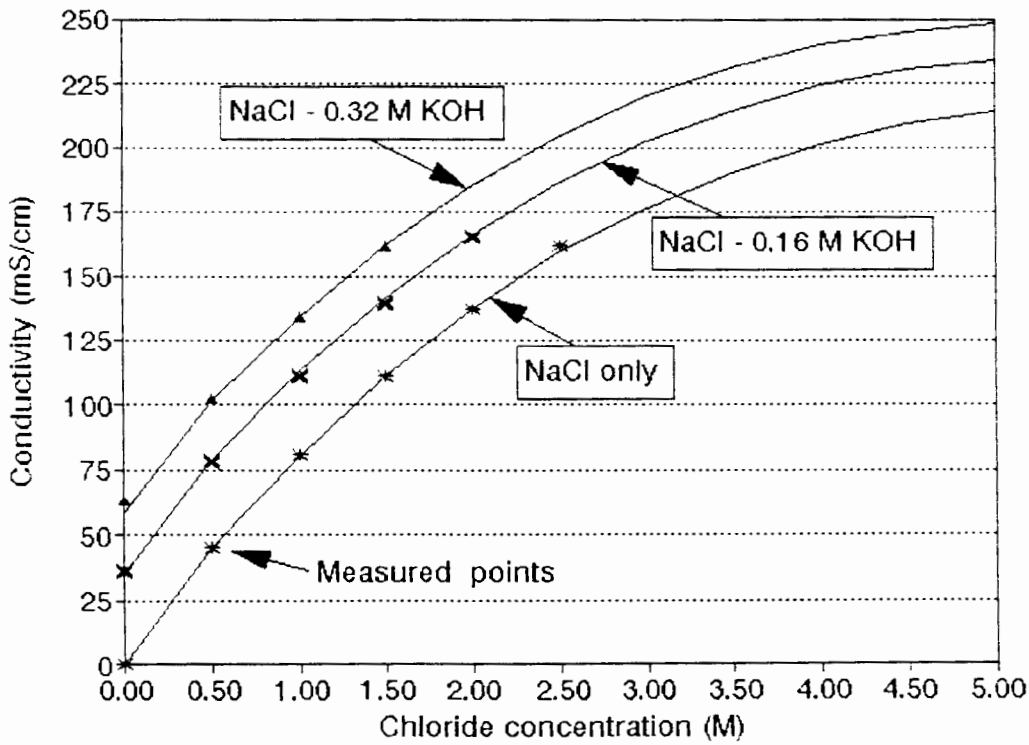

Figure 6.6: Conductivities of NaCl and NaCl-KOH combined solutions.

There was a good correlation between the calculated and observed conductivities of the different NaCl solutions (see tables 6.5 and 6.6 and figure 6.6). The addition of different levels of KOH increased the conductivity by an amount that decreased with an increase in NaCl concentration due to the change in viscosity of the solution (figure 6.6). The percentage increase in conductivity is smallest at the highest NaCl concentration. Using a high concentration NaCl solution in the conductivity test would therefore minimize the effect of a variable concrete pore solution composition. With the 5 M NaCl solution a 0.16 M KOH content caused an 8 % increase in conductivity and a 0.32 M KOH content caused a 14 % increase in conductivity.

6.6.1.4 Conductivities of cement mortar specimens saturated with concentrated solutions

The conductivities of nominally identical mortar samples (cored from the same specimen) saturated with NaCl solutions of various concentrations were determined using the conductivity test. The diffusibility ratio (Q) was calculated for three different assumed values of σ_o. This was done to demonstrate the sensitivity of Q to σ_o at different chloride concentrations.

Experimental Procedure

Sample preparation

Ordinary Portland cement (OPC) mortars were made with a water/cement ratio of 0.5 and a sand/cement ratio of 1.83. The mortar was mixed in a mechanical mixer for 3 minutes and then poured into 42 mm diameter x 160 mm moulds. The mortar filled moulds were vibrated for 30 seconds and then re-vibrated after an hour for another 30 seconds. After 24 hours the mortar cylinders were removed from the moulds and placed in a curing tank at 23 °C. After 3 days moist curing 10 mm thick discs were sliced from the cylinders using a diamond saw. The top 10 mm from the as-cast surface was discarded. The discs were then oven dried at 50 °C for 48 hours (constant mass) and then epoxied into PVC collars.

Saturated conductivity test

The mortar specimens were vacuum-saturated in a saturated $Ca(OH)_2$ solution for 3 hours and the conductivity determined using the conduction test.

NaCl conduction test

The specimens were again oven dried for 48 hours at 50 °C and left to cool before the second saturation with the various NaCl solutions. Although oven drying would affect the pore structure, each specimen was dried for the same period at the same temperature so that this effect was uniform. The second saturation involved placing the specimens in the respective solutions for 24 hours. The conductivity was determined using the conduction test.

Normalisation of results

To reduce the effect of differences in pore structure (in terms of conductivity) of the various specimens, the results were normalised using a correction factor based on the $Ca(OH)_2$ solution saturated conductivity of each specimen.

Each mortar specimen was tested twice. The first test was a $Ca(OH)_2$ solution saturated conductivity test, followed by oven drying, and the second test was a NaCl saturated conductivity test. Since each specimen was derived from the same mortar cylinder, all had a similar pore solution. The variation in the saturated conductivities (CV = 10 %) could therefore be ascribed to slight changes in the pore structure. To eliminate these slight changes, the results were normalised by a factor calculated as follows:

$$NF_i = \sigma_{sat,i} \,/\, \text{mean } \sigma_{sat}$$

where NF ... normalising factor

σ ... conductivity [mS/cm]

The NaCl saturated tests, which were done at various NaCl concentrations, produced results which were then corrected using this factor:

$$\text{normalised } \sigma_{NaCl,i} = \text{measured } \sigma_{NaCl,i} \,/\, NF_i$$

The conductivities of the mortar specimens saturated with different NaCl solutions were measured, and divided by the correction factor to obtain the normalised NaCl conductivity (see table 6.7). The data was plotted on a graph (see figure 6.7). A polynomial curve was fitted to the data (least squares method), neglecting the third and fourth points. The resulting curve fitted well to all the other points.

The resistivity of concrete is mainly governed by the level of metal alkali ions (K^+ and Na^+) since the conductivities of KOH and NaOH are much greater than $Ca(OH)_2$ at high

concentrations (0.1 M - 1 M). This is because of the low solubility of $Ca(OH)_2$ and the higher mobilities of K^+ and Na^+. Most concretes are saturated in $Ca(OH)_2$ but the level of alkali ions can vary significantly.

Table 6.7: Conductivities of NaCl saturated mortar samples.

Concentration [M]	Measured $\sigma_{sat,i}$ [mS/cm]	NF, correction factor	Measured $\sigma_{NaCl,i}$ [mS/cm]	Normalised $\sigma_{NaCl,i}$ [mS/cm]
0.5	0.494	1.03	0.96	0.93
1.0	0.450	0.94	1.18	1.26
1.5	0.550	1.15	1.77	1.54
2.0	0.449	0.94	1.95	2.07
2.5	0.444	0.93	2.08	2.24
3.0	0.390	0.81	2.01	2.48
3.5	0.566	1.18	3.10	2.63
4.0	0.501	1.04	2.96	2.85
5.0	0.471	0.98	2.96	3.02
0.0	mean: 0.479			

The rate of increase in conductivity is reduced at higher concentrations (see figures 6.6 and 6.7) mainly because of the increase in viscosity of the solutions (see equation 6.3).

The actual pore solution conductivity (σ_o) of the mortar specimens was not known. The values of the artifial solutions (6.6.1.3) were therefore used to calculate Q. These solutions contain a range of KOH levels (0 - 0.32 M). Results are given in figure 6.8.

From the figure it is clear that at high NaCl concentrations, the diffusibility ratio (Q) is not sensitive to the assumed KOH content in the pore solution. In contrast, at low NaCl concentrations, the diffusibility ratio is very sensitive to the assumed KOH content in the pore solution. Therefore, when a high concentration chloride saturating solution is used, the measured conductivity is directly proportional to the diffusibility ratio. However, when a low

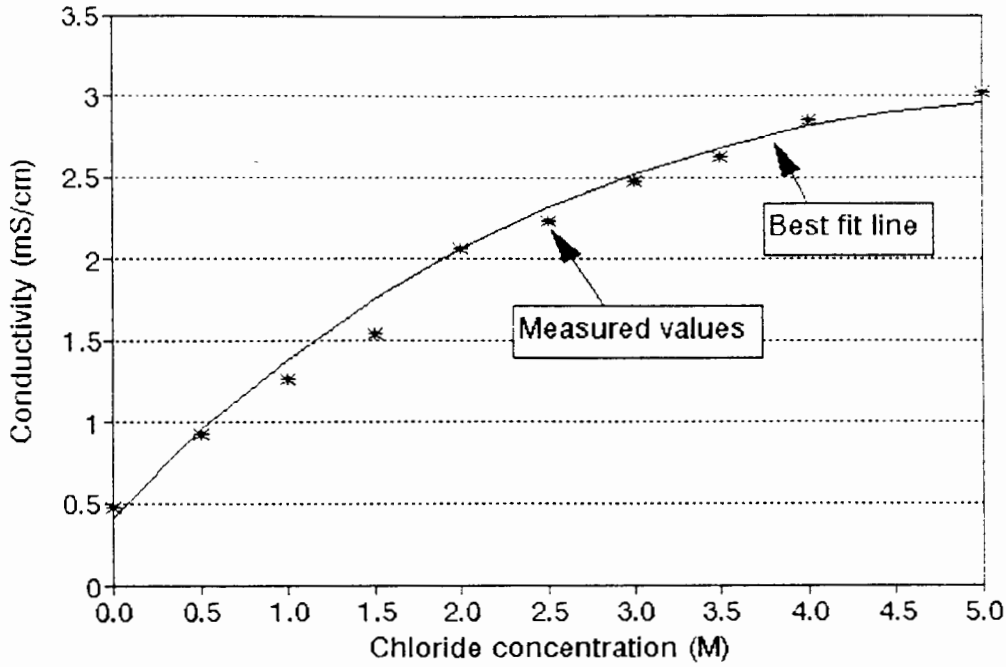

Figure 6.7: Conductivities of NaCl saturated mortar samples (w/c = 0.5).

concentration chloride saturating solution is used, the measured conductivity is a function of both the diffusibility of the material, and the initial pore solution conductivity of the material.

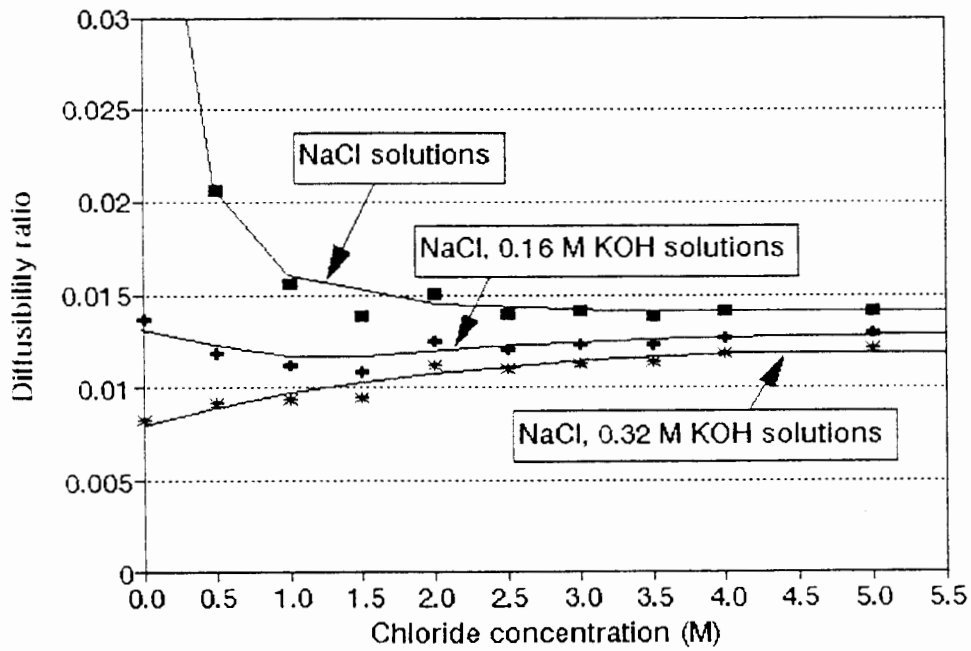

Figure 6.8: Diffusibility ratios.

$$\sigma \propto Q \qquad for\ [Cl^-] > 3\ M$$

$$\sigma = f(Q, \sigma_0) \qquad for\ [Cl^-] < 3\ M$$

6.6.1.5 Conclusions.

1. The conductivity part of the diffusibility relationship ($Q = \sigma/\sigma_0$) remained sensibly constant at higher chloride concentrations (> 3 M) regardless of the assumed levels of KOH in the pore solutions. In contrast, at low NaCl concentrations, the diffusibility ratio was found to be very sensitive to the assumed KOH content in the pore solution.
2. Saturating concrete or mortar specimens with highly conductive (5 M NaCl) solution would reduce the variation in the pore solution conductivity of different concrete or mortar specimens.
3. Resistivity values (water-saturated) will be affected by the alkali content of a concrete, and will therefore not always be inversely proportional to the diffusibility (or diffusivity) of concrete. (This will only be true in cases where the same materials are used).

6.6.2 Sample conditioning

6.6.2.1 Oven drying

Two oven drying temperatures, 50 °C and 100 °C were considered. During the series 2 tests, the mass loss of concrete specimens (68 mm Ø x 25 mm) from two mixes (Mix 6: 40 MPa PC and mix 7: 60 MPa PC - series 2 tests: Appendix 2) were measured at 50 °C for 14 days and then at 100 °C from 14 to 21 days (see figure 6.9).

The samples took approximately 14 days to reach constant mass at 50 °C. The moisture loss at 7 days was between 90 and 95 % of the moisture loss at 14 days. At 100 °C drying was more rapid, and an additional 1 % moisture with respect to the dry mass of the sample was removed.

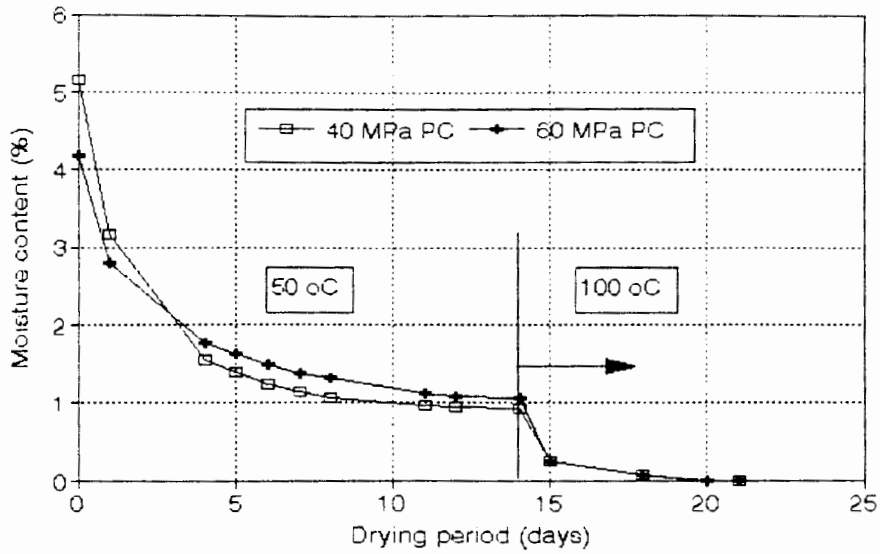

Figure 6.9: Drying at 50°C and 100 °C.

Tests were conducted to determine to what extent oven drying at 50 °C and 100 °C would affect the conductivity of concrete samples since it has been shown that oven drying can damage the pore structure of concrete. For example, Konecny and Naqvi (1993) showed that the pore size distribution of blended cement mortars was affected by oven drying at 105 °C. The measurements were done using mercury intrusion porosimetry.

Pigeon et al (1993) determined the effect drying had on the chloride permeability of normal portland cement and silica fume concretes. After 7 days of moist curing the mixes were dried at 23 °C, 38 °C and 110 °C for 28 and 90 days, and tested using the AASTHO T277 rapid chloride permeability test. In most cases drying at 110 °C dramatically increased the chloride permeability of the samples, compared with drying at 23 °C. In contrast drying for 28 days at 38 °C did not increase the chloride permeability of the samples. It was accepted that the concretes continued curing during the drying phase and that the higher temperature of 38 °C would have improved hydration initially. This could have masked the damaging effects of drying. It is also known that drying at any temperature (ie. 23 °C as well) causes damage to the concrete in the form of microcracking.

The tests conducted in our laboratory were part of a series of tests used to study the effect of the reduction in conductivity in the presence of chloride ions (see section 6.7). 40 MPa 50 % slag concrete wet cured for 12 months was used for this series of tests. Four specimens

(68 mm Ø x 25 mm) were dried at 50 °C for 7 days (< 20 % R.H.), and four were dried at 105 °C for 7 days. The specimens were vacuum-saturated with a $Ca(OH)_2$ solution for 5 hours and left immersed in the solution at 25 °C. The conductivities were measured after 3, 7, 14, 28 and 56 days.

The results are plotted in figure 6.10. The following observations were made.

1. At 3 days after saturation, the 105 °C dried specimens had a 50 % higher conductivity compared with the 50 °C dried specimens. This indicates that much greater damage was caused at the higher temperature.
2. The conductivity of both sets of specimens reduced with time. The conductivity of the 105 °C dried specimens reduced more rapidly and converged to the level of the 50 °C specimens after 28 days. This was most likely caused by autogenous healing which indicates that at 50 °C some damage was also caused.

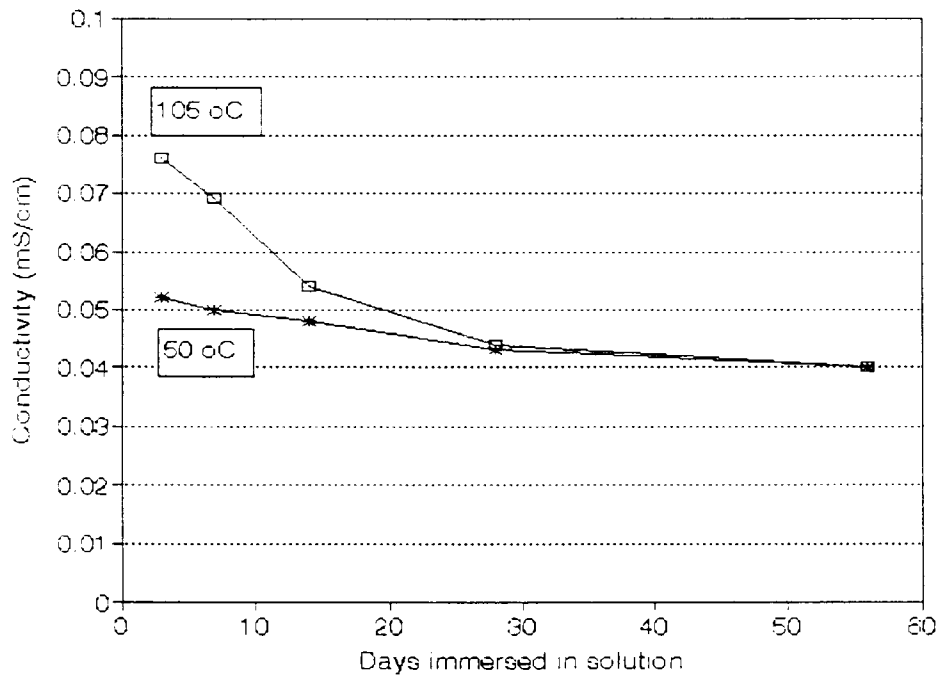

Figure 6.10: Conductivity of concrete saturated with sat. $Ca(OH)_2$ solution after drying at 50 °C and 105 °C plotted against time.

Drying at any temperature will cause damage, and concrete on site would be susceptible to damage due to drying, particularly in the South African environment.

A drying regime of 7 days at 50 °C was chosen for the conductivity test. This is a reasonable compromise between excessive damage at 105 °C, and a too long a period of drying at less than 50 °C. Existing durability index tests used in our laboratory (oxygen permeability and water sorptivity tests (Ballim, 1993) also use this drying regime. Further work was done in chapter 7 which deals with drying at 7 and 14 days at 50 °C.

6.6.2.2 Vacuum saturation procedure

Concrete specimens of size 68 mm by 25 mm reached constant mass in the saturation procedure after approximately 2 hours, however this does not necessarily verify the saturation procedure. Tests on concretes of various thicknesses (15 - 30 mm) were therefore conducted to verify the saturation procedure (see section 6.6.3).

6.6.3 Thickness tests

The thickness tests involved testing a number of concrete specimens (obtained from the same concrete sample) with a range of thicknesses. The objective of these tests was to verify a number of aspects of the chloride conduction test:

1) The validity of the conductivity relationship, $\sigma = it/VA$ ie. $i \propto 1/t$ (for constant σ).
2) The effectiveness of the saturation procedure.
3) The effect of coarse aggregate size relative to specimen size.

The tests were also used to determine the coefficients of variation of the conductivity determinations at the various thicknesses and at the different times of immersion in the chloride solution to obtain the optimum conditions for the test.

The concrete specimens were obtained from 50 MPa OPC (w/c = 0.44) concrete beams (500 x 100 x 100 mm). The nominal size of the coarse aggregate was 19 mm. The concrete beam was demoulded after 24 hours, wet cured for another 6 days, and then cored. The as-cast surfaces of the cores were removed by slicing off 10 mm. The cores were then sliced at four nominal thicknesses of 15, 20, 25 and 30 mm. There were six each of the 15, 20 and 30 mm thick specimens, and three of the 25 mm thick specimens. The chloride conductivities were determined after 5 hours vacuum saturation and again after 1, 3 and 7 days immersion in the chloride solution (5 M).

The conductivity determinations are shown in table 6.8. The mean results are plotted in figure 6.11. The lowest variation in test determinations (C.V. = 6.73 %) was observed with the 1 day specimens. It was therefore decided to use a similar saturation procedure (5 hours vacuum saturation + 18 hours immersion in the chloride solution) in the standard test method.

The results also show a reduction in chloride conductivity with time. This reduction was ascribed to additional hydration, the possible pore blocking effects of chloride binding and a reduction in pore solution conductivity. This effect is dealt with in more detail in section 6.6.

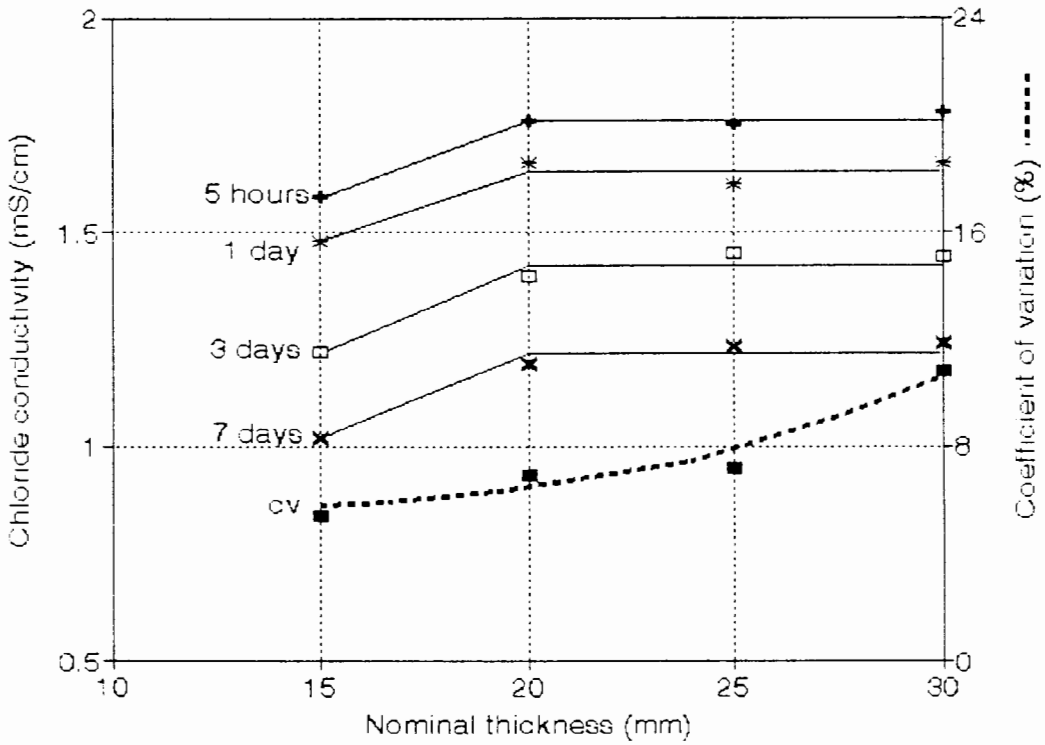

Figure 6.11: Effect of specimen thickness on conductivity and variability.

The chloride conductivity results of the concrete samples remained sensibly constant for 20, 25 and 30 mm thicknesses. The lower conductivity of the 15 mm sample was ascribed to voltage losses between the Luggin capillaries and the concrete specimen. These losses became significant for two reasons:

1) The distance between the tubes and the specimen surfaces was the greatest with the 15 mm specimens.
2) The ionic flux (electric current) through the 15 mm specimens was higher relative to

Table 6.8: Thickness test results.

Nominal thickness of specimen (mm)	Chloride conductivity (mS/cm)			
	5 hours vacuum saturation	1 day in solution	3 days in solution	7 days in solution
15	1.53	1.41	1.31	1.08
	1.63	1.49	1.24	1.00
	1.65	1.58	1.22	1.12
	1.61	1.50	1.24	1.04
	1.58	1.45	1.14	0.94
	1.48	1.44	1.14	0.93
Mean	1.58	1.48	1.22	1.02
C.V. (5.4 %)	4.03%	3.94%	5.30%	7.64%
20	1.61	1.57	1.40	1.09
	1.64	1.55	1.35	1.24
	1.87	1.71	1.42	1.30
	1.74	1.75	1.50	1.20
	2.01	1.83	1.34	1.19
	1.66	1.54	1.38	1.12
Mean	1.76	1.66	1.40	1.19
C.V. (6.9 %)	8.95%	7.34%	4.08%	6.52%
25	1.92	1.58	1.33	1.21
	1.67	1.57	1.43	1.17
	1.65	1.67	1.59	1.32
Mean	1.75	1.61	1.45	1.23
C.V. (7.2 %)	8.69%	3.39%	8.95%	6.27%
30	1.90	1.70	1.18	1.18
	1.78	1.45	1.24	1.11
	1.89	1.76	1.49	1.25
	1.81	1.68	1.41	1.19
	1.65	1.50	1.67	1.19
	1.64	1.85	1.67	1.52
Mean	1.78	1.66	1.44	1.24
C.V. (10.8 %)	6.23%	9.13%	14.57%	11.61%
Overall mean	1.72	1.60	1.38	1.17
Combined C.V.	7.03%	6.73%	9.21%	8.54%

the thicker specimens, hence the potential gradient in the adjacent solutions was greater. The conductivity (σ) of a homogenous material should be constant irrespective of the thickness of the specimen tested. Therefore the concrete specimens in the thickness range 20 - 30 mm appear to behave as a homogenous material.

There was no evidence from the results to indicate that the coarse aggregates (nominal 19 mm) influenced the measured property (15 - 30 mm thick specimens). Aggregate paste interfaces (which may have a higher porosity compared with the bulk paste) were expected to increase the chloride conductivity results of the thinner specimens where coarse aggregates were more likely to span the entire specimen thickness. Note however that with diffusion and conduction, ionic flow is proportional to the cross-sectional area ($\propto r^2$) of the diffusion path, while with permeation in contrast, the flow is proportional to r^4 due to frictional effects (D'Arcy's law). This implies that with permeation, the flow predominantly follows the larger passages, while with diffusion and conduction, even the smallest passages contribute significantly to the total flow of ions. The effect of aggregate-paste interfaces are therefore more likely to be manifested in a permeation test compared with a diffusion or conduction test.

The results also proved that the saturation procedure was adequate for this specific concrete in terms of the conductivity results. However, in terms of the inherent sample variation there was some indication that the saturation procedure was not perfect. The variability generally increased with the thicker specimens (see figure 6.11, dotted line). With perfect sample conditioning, variability is more likely to decrease with an increase in thickness due to the composite nature of concrete.

With high strength pozzolanic mixes, it would prove more difficult to saturate the specimens. In this case the test results might well be influenced by an inadequate saturation procedure. The vacuum saturation procedure could be improved by applying a vacuum on the specimens for 3 hours before the saturating solution is added (ASTM C1202-91). The air within the specimens could then be evacuated more readily, and an increased vacuum level could be utilised. With the solution in the chamber the vacuum is constantly reduced by the evaporation of water as the solution boils. The vacuum pump is also adversely affected when water vapour is evacuated for prolonged periods of time.

When there is doubt whether the saturation procedure is satisfactory, the testing of different specimen thicknesses is suggested. A lower conductivity in the thicker specimens would indicate inadequate saturation. More work is required to demonstrate the limitations of the test with regards to saturation.

6.7 REDUCTION IN CHLORIDE CONDUCTIVITY WITH TIME

The thickness tests indicated that the conductivity of the concrete specimens tested using the chloride conductivity test reduced with time if left immersed in the chloride solution (see figure 6.11). This phenomena was observed with the modified Dundee test as well (see chapter 5), and prompted two questions:

1) Does this factor influence the chloride conductivity test ?

   The objective of the chloride conductivity test is to measure the physical resistance of concrete to chloride ingress, since chloride ingress formulae include this parameter (steady state diffusion coefficient) explicitly. The test should therefore ideally exlude additional factors such as chloride binding. In the modified Dundee test, the factors causing a reduction in conductivity are likely to influence the maximum current measured since the chloride ions are present inside the specimen for a significant period (approximately 7 days) before quasi-steady state conditions are reached. In the proposed chloride conductivity test, this period is reduced to 23 hours, however it is still necessary to determine the relative effect during this period.

2) Can the measured reduction be used as a measure of the chloride binding characteristics of concrete ?

   In the series 2 tests (see appendix), the reduction in chloride conductivity after 2 weeks immersion in chloride solution was determined to give some indication of the chemical resistance of concrete to the transport of chloride ions. Mackechnie (1996) found that by adjusting chloride conductivity values using reduction factors based on the reduction in chloride conductivity with time, correlations with in-situ chloride ingress were improved substantially. However, the reductions measured could be as

a result of a number of factors (see below), all of which might not be relevant to the process of chloride ingress.

Three probable factors causing the reduction in conductivity were considered and their implications are discussed below. They are: Changes to the physical pore structure due to the presence of chloride ions, changes to the pore solution conductivity due to chloride binding and additional hydration.

6.7.1 Changes to the physical pore structure due to the presence of chloride ions

Work done with the Dundee (1990) rapid chloride test (see section 5.5) indicated the possibility that the presence of chloride ions could change the diffusibility of the material. The decrease in steady state current exceeded the rate expected should hydration have been the only factor (Streicher et al, 1994). (Note that a reduction in pore solution conductivity (6.7.2) is not present in the Dundee test since a continuous flux of ions through the specimen would prevent this).

It is well known that cement-based materials can bind chloride ions, and thereby reduce the apparent chloride diffusivity of the material. However not much is known whether the presence of chloride ions can change the physical pore structure.

Midgely and Illston (1984) showed with mercury intrusion porosimetry (MIP) tests that the presence of chloride ions (externally derived) reduced the size of the pores of the highest frequency of occurence. No significant change in the quantity of hydrates could be measured (ie. the presence of chlorides did not accelerate hydration), so it was suggested that the reduction in pore size was due to the formation of calcium chloride on the surface of the CSH. Kayyali and Haque (1988) reported that difficulty was experienced with the process of porewater expression for specimens which were immersed in a sodium chloride solution for 90 days compared to similar specimens cured in a fog room, indicating a decrease in water permeability when chloride ions are present.

Suryavanshi et al (1995) showed with MIP tests that the addition of chlorides to OPC and SRPC mortars during mixing reduced the total accessible pore volume compared to

corresponding chloride-free mortars. They stated that the quantity of chloride ions bound by CSH gel would not alter the microstructure sufficiently to cause the observed effects, based on work by Lambert et al (1985). From this, they deduce that the possibility of chemisorption of the chloride ions on the surface of the CSH gel which modifies the pore size distribution seems remote. They ascribed the reduction in accessible pore volume to a change in the morphology of the CSH gel. SEM micrographs showed the needle-like structure of the CSH gel for the chloride free mortars, while the mortars in the presence of chloride ions had a much more dense structure. It was not clear from the literature whether the ingress of externally derived chloride ions into mature concretes would have the same effect.

Thus in summary, a number of researchers have identified a change in concrete pore structure due to the presence of chloride ions, but they disagree on the exact mechanisms involved in this change.

Although Suryavanshi did not believe the quantity of chloride ions bound would alter the microstructure, it might be the case with the chloride conduction test where a high concentration (5 M) chloride solution is used.

In any event, even if the reduction in conductivity is caused by changes in the physical pore structure due to the presence of chloride ions, it still does not prove that this factor is significant in the case of in-situ chloride ingress since much lower chloride concentrations are generally involved (sea water - 0.5 M).

6.7.2 Changes to the pore solution conductivity due to chloride binding

Chloride binding would remove chloride ions from solution and thereby reduce the conductivity of the pore solution.

Referring to section 6.5.1.3, it can be shown that a 35 % reduction in chloride concentration from 5 M NaCl to 3.25 M results in only about a 14 % reduction in conductivity (see figure 6.6) due to the non-linear relationship between concentration and conductivity at high concentrations. The typical reductions measured in the series 2 tests (Appendix) were

substantially higher (44 % - 77 %). This would seem to indicate that the reduction in pore solution conductivity has a minor influence. However, the possibility exists of increasing this factor (reduction in pore solution conductivity) and reducing the first factor (changes in physical pore structure) by using a lower concentration chloride solution eg. 1 - 3 M. This is desirable as chloride binding capacity can then be determined from the reduction in conductivity of the concrete.

Note that the mechanism whereby chloride binding affects in-situ chloride ingress (non-steady state diffusion) differs from the mechanism whereby it affects conductivity. A number of chloride ingress formulae take account of binding explicitly (see Chapter 3), hence it would be useful if the binding capacity could be determined from the reduction in conductivity in the chloride conductivity test.

6.7.3 Additional hydration

Additional hydration would change the physical pore structure in such a way as to reduce conductivity.

In Appendix 2 - Part A table 7 it can be seen that differences in reduction percentages between samples cured for shorter periods before re-saturation for the conductivity test, and those cured for a full 28 days, are relatively small, except possibly for the GGBS mixes. In contrast, the OPC mixes which were insensitive to initial curing showed a substantial reduction in chloride conductivity. This would seem to indicate that additional hydration from delayed curing has a minor influence relative to the first two factors.

6.7.4 Effect of reduction on the chloride conductivity test

The chloride conductivities of two concretes, 50 MPa OPC (thickness tests, section 6.5) and 40 MPa 50 % slag blend (series 2 tests, mix 26), are plotted against time in figure 6.12. The concretes were left immersed in the 5 M NaCl solution between the tests. By extrapolating from 1 day back to 0, it can be seen that the possible reduction occuring during this time varies between 8 - 15 % relative to the 1 day result. Note also that unlike the Dundee test, all concretes are tested at 23 hours (after 5 hours vacuum saturation + 18 hours immersed).

This effect is therefore unlikely to bias certain cements.

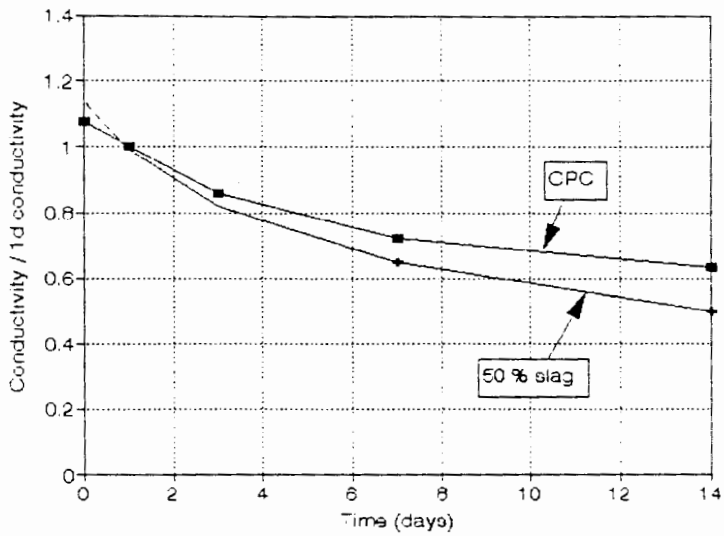

Figure 6.12: Reduction in conductivity of OPC and 50 % slag concretes.

6.7.5 Tests on mature concrete using different concentration chloride solutions

Tests with different concentration chloride solutions were conducted to determine which mechanism (physical pore blocking effect (6.7.1) or chemical reduction in pore solution conductivity effect (6.7.2)) dominates. Concrete specimens wet-cured for 1 year were chosen to virtually eliminate the effect of additional hydration.

The concrete specimens chosen were from a 40 MPa 50 % slag mix (series 2 tests, mix 26). The reductions measured initially for this mix (28 day old specimens + 14 days in saturating solution) were 77 % (1 day wet cured), 70 % (7 days wet cured) and 63 % (28 days wet cured) (Appendix 2, series 2 tests, table 6).

From figure 6.13 it can be seen that after 14 days immersion in the 5 M NaCl solution (365 day old specimens + 14 days immersion), there was a 50 % reduction in conductivity. This implies that the extra 13 - 27 % (63 to 77 - 50 %) measured initially (Appendix 2, series 2 tests, Part A) was due to additional hydration.

Two saturating solutions, 5 and 3 M NaCl, were chosen (see figure 6.13). The pore blocking

effect should increase with concentration, as the volume of bound and precipitated products increase with an increase in concentration of the saturating solution. In contrast, the reduction in pore solution conductivity effect should increase with a decrease in concentration. This is due to the more linear relationship between conductivity and concentration at lower concentrations (see figure 6.6).

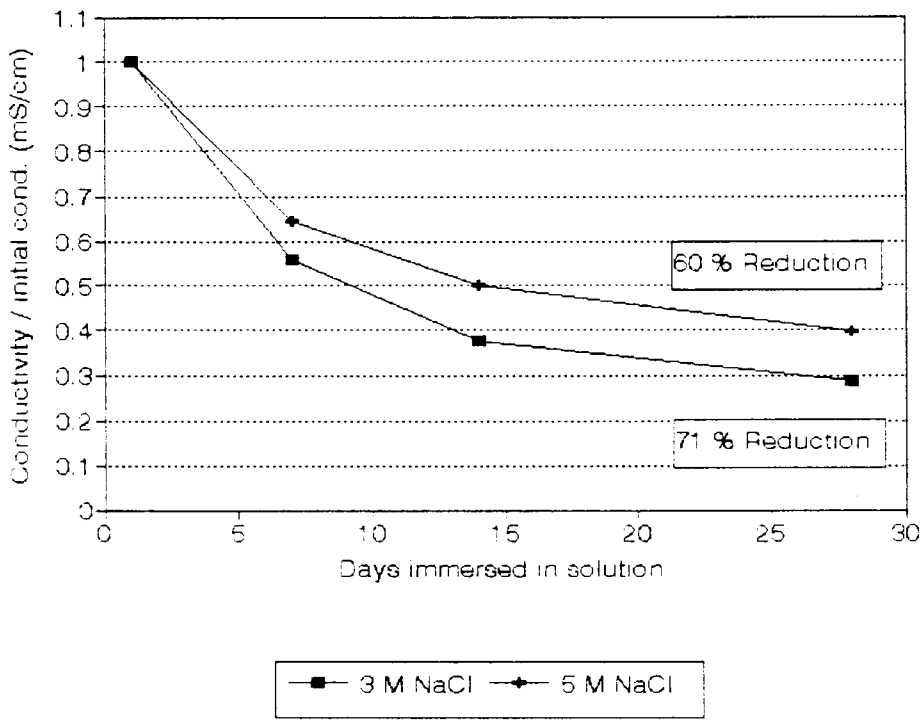

Figure 6.13: Ratio of chloride conductivity to initial chloride conductivity versus days immersed in chloride solution (3 M and 5 M NaCl.

The reduction in conductivity after 28 days immersion was 60 % for the 5 M solution and 71 % for the 3 M solution (figure 6.13). Assuming that the reduction is only due to the depletion of chloride ions, it was calculated that 78 % and 80 % of the chloride ions were bound respectively (from figure 6.6).

The increase in reduction percentage with a decrease in concentration indicates that the effect of the reduction in pore solution conductivity is the dominant mechanism. It also indicates that a very high percentage of ions are bound.

6.7.6 Proposed chloride binding test

The chloride conduction test determines mainly the physical resistance of concrete to chloride ingress due to the short duration of the test. Chloride ingress on-site (non-steady state chloride diffusion) is strongly influenced by the chemical resistance (chloride binding effects) of concrete to chloride ingress. Current tests which measure the chloride binding characteristics of concrete (pore expression tests) require expensive and specialist equipment and are not suitable for routine laboratory tests. The need for a suitable laboratory test that characterises the chemical resistance of concrete to chloride ingress is evident.

The reduction in chloride conductivity was shown to be very pronounced at lower chloride concentrations (3 M). This is due to the more linear relationship between conductivity and concentration at lower concentrations (figure 6.6). The reduction percentage could be correlated to the bound percentage which can be determined using a pore expression apparatus (mortar samples). Work will be required to determine an ideal concentration chloride solution for the purposes of the test.

The test procedure would involve the following steps:

1) Sample preparation as with the chloride conduction test.
2) Sample conditioning as with the chloride conduction test except for using a 3 M saturating solution.
3) Testing as with the chloride conduction test except for using a 3 M cell solution.
4) Immersion in the saturation solution for two weeks.
5) Retesting in the chloride conduction test apparatus.
6) Converting the reduction in conductivity to a chloride binding capacity using the correlation study described above.

The proposed binding test would be more practical for routine testing compared with the pore expression method. It could also be used on concrete (the pore expression apparatus is only suitable for tests on cement mortar or paste).

6.8 CONCLUSIONS

6.8.1 Chloride conduction test

A test that measures the physical resistance of concrete to the transport of chloride ions was developed. The main advantages of the test in relation to existing test methods are presented below:

- As far as can be ascertained, the test is the most rapid of all chloride tests developed to date. It is the only test that measures the physical resistance of concrete to chloride ingress using one single measurement after sample conditioning.
- The test has a sound theoretical basis and measures the required property in the absence of outside influences. The use of the high concentration chloride solution (5 M NaCl) to saturate the concrete specimens ensures the standardisation of the concrete pore solution conductivity, hence the conductivity measurement of the specimen is directly related to the steady state chloride diffusivity of the concrete.
- The test is of low cost, and is easy to use. The test apparatus uses a silicone rubber collar which mechanically clamps the concrete specimens to allow rapid changeover from one sample to another.

Further advantages of the test will become evident in chapter 7 which deals with the standardisation and the precision of the test method.

The characteristics of the test make it suitable for:

- durability research.
- prediction of chloride ingress.
- construction quality control.

These aspects are dealt with in chapters 8 and 9.

6.8.2 Proposed chloride binding test

A reduction in chloride conductivity after the initial chloride conductivity test was measured if the specimens were kept immersed in a 5 M NaCl solution. At this high concentration the test is not that sensitive to a reduction in chloride concentration in the pore solution (due to

chloride binding) and is more likely to be influence by pore blocking effects (due to interactions between the cement and the chlorides). It was shown that when a lower concentration (3 M NaCl) solution is used, the test becomes very sensitive to any reduction in the chloride concentration in the pore solution while the likelihood of pore blocking effects is reduced.

A rapid chloride binding test was proposed which measures the reduction in conductivity of a concrete sample saturated with a suitable chloride solution. The test can easily be verified with pore expression tests.

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CHAPTER 7

STANDARDISATION OF THE CHLORIDE CONDUCTION TEST

7.1 INTRODUCTION

Ideally, if the same material is tested in different laboratories, the same test results should be obtained. This requires a valid and well-written standard test method that has been developed in one competent laboratory and has been subjected to a screening procedure (ruggedness test). It also requires appropriately designed apparatus for the test.

The development of the test (chapter 6) involved determining the optimum conditions for the test. However, in order to write a suitable standard test method, it is necessary to consider the sensitivity of the test to environmental factors. A ruggedness test was therefore conducted to determine to what degree the conditions specified in a test method must be controlled. The standard test method including a detailed design of the test apparatus was then prepared.

A standard test method should state the precision of the test. Users of the test can then determine whether a given series of results can be considered valid, whether an operator is qualified to perform the test in question, and whether a laboratory is qualified to perform the test in question. Ideally, an interlaboratory test programme (such as specified in ASTM C802-87) is required to determine the precision of a test method. At the time of completing this thesis, the test was not sufficiently widely used to allow the implementation of an interlaboratory test programme. However, an attempt was made to meet most of the criteria required for an interlaboratory study.

The objectives of this chapter were to standardise the test procedure and to determine precision indices for the test. The scope of this chapter was the conduction of a ruggedness test programme, the writing of the standard test method and the statistical analysis of results obtained in the series 2 tests.

7.2 RUGGEDNESS TEST

The ruggedness test is used to determine to what degree the conditions specified in a test method must be controlled. This test uses a statistically designed series of experiments to

determine whether a measurement process is sufficiently rugged to withstand small changes in operating conditions when it is run in different laboratories (Popovics, 1982, p.20). A ruggedness test of a test method should precede an interlaboratory study.

A ruggedness test is conducted by making systematic changes in the variables associated with the test method and observing the size of the associated changes in the test method results. A t-test is then used to judge if a variable is statistically significant relative to the measurement variability.

The first step is to identify the main factors that might affect the test result. It is not always possible to include all the factors that affect the test result in the test relationship. For example, the test relationship might exclude temperature although the measured property is related to it. In this case, the test method usually prescribes a fixed temperature for the test. The ruggedness test is used to determine to what degree the temperature or other factors need to be controlled so that these effects are insignificant relative to the measurement variability.

The ruggedness test described in ASTM 1169 has a capacity of seven factors. The seven most important factors must be selected for the test. The test can then be repeated with a new set of factors if there is a need.

7.2.1 Factors affecting the chloride conduction test

The variables or 'factors' associated with the chloride conduction test are the following:

Variables included in the test relationship:

1) Applied voltage.
2) Measured current.
3) Sample thickness.
4) Surface area of sample.

Variables excluded from the test relationship:

5) Concentration of saturating solution.
6) Temperature.

Factors affecting the assumed conditions of the test:

7) Concentration of cell solution.
8) Time of oven drying.
9) Time of vacuum saturation.
10) Time immersed before test.
11) Time of reading after voltage is applied.

The conductivity relationship includes the first four variables. This relationship is a fundamental electrochemical relationship (see chapter 3) and the relationship as such need not be verified. The thickness tests (see chapter 6) verified that the conductivity relationship governs the test. These variables will therefore be excluded from the ruggedness test.

The required accuracy of the voltmeter, ammeter and vernier calliper will be specified in the standard test procedure. This will be done to ensure that any error resulting from these factors is also negligible compared with the inherent sample variability.

The remaining factors will be tested in the ruggedness test:

5) and 6) Concentration of saturating solution; Temperature.

The conductivities of solutions are related to ionic concentration and temperature. In the test method, 'chloride conductivity' is defined as the dc conductivity of an initially dry concrete sample saturated with a 5 M NaCl solution at 25 °C. It is expected that strict control will be needed over these two factors.

7) Concentration of cell solution.

Ideally the test results should be independent of the conductivity of the cell solutions. The test apparatus was designed to achieve this (by using Luggin capillaries). This variable is included in the ruggedness test to verify that the test results are for all practical purposes independent of the cell solution conductivity.

8) and 9) Oven drying; Vacuum saturation.

The test method assumes that the concrete samples are sufficiently dry after oven drying, and sufficiently saturated after the vacuum saturation as not to affect the test result. Incomplete drying could lead to the dilution of the saturating solution which would reduce the conductivity of the sample. Incomplete saturation could also lead to a decrease in conductivity. Note that drying and saturation times are dependent on

the specimen size and the quality of the concrete. The ruggedness test results therefore only apply for specimens of size 68 mm in diameter and 25 mm in thickness and of similar quality.

10) Immersion time.

The saturated concrete will continue to cure, resulting in a more refined pore structure. Chloride ions will also be bound by the cement, removing them from solution, and possibly affecting the pore structure. All these factors will reduce the conductivity of the concrete.

11) Reading time.

Although the test is a steady state test, the test apparatus has not been designed to maintain the steady state conditions for very long. This would have required cells with larger volumes, stabilisation of the pH in the cell solutions, and control over the temperature inside the cells.

7.2.2 Experimental procedure

The "Plackett-Burman" design (ASTM E 1169-89) with two levels (high-low, on-off) per variable was used in this series. This design requires the simultaneous change of the levels of all of the variables, and allows the determination of the separate effects of each of the variables on the measured results.

The design assumes that the effect for each variable is independent of the effects of other variables. As a guide the high and low settings of the factors should represent the extreme limits that may be expected to be observed between different qualified laboratories. Small or moderate changes between the high and low settings will reduce interactions, however the changes should be large enough relative to the measurement error.

The seven factors that were studied are listed below:

Factor A - Concentration of saturating solution, 5 M or 4.5 M.

Factor B - Temperature, 25 °C or 22 °C.

Factor C - Concentration of cell solution, 5 M or 1 M.

Factor D - Oven drying, 7 days or 14 days.

Factor E - Vacuum saturation, 5 hours or 2 hours.

Factor E - Vacuum saturation, 5 hours or 2 hours.

Factor F - Immersion time, 18 hours or 0 hours.

Factor G - Reading time, 0 min or 2 min.

The experimental design is shown in table 7.1. Each test has a unique set of conditions. The effects of the different factors are separated later. This method is very efficient compared to testing the factors independently which would have required $2^7 = 128$ tests.

Table 7.1: Experimental design.

Test No.	Factor						
	A (M-sat)	B (°C)	C (M-cell)	D (dry - (d))	E (vac - (h))	F (imm - (h))	G (read - (min))
1	5	22	1	7	2	0	2
2	5	22	5	7	5	18	0
3	5	25	1	14	2	18	0
4	5	25	5	14	5	0	2
5	4.5	22	1	14	5	0	0
6	4.5	22	5	14	2	18	2
7	4.5	25	1	7	5	18	2
8	4.5	25	5	7	2	0	0

Mix Design:

Since the effects of the different factors are compared with the measurement variability, care was taken to reduce the inherent sample variability.

A 40 MPa OPC concrete mix was designed for a slump of 50 mm. Cape flats dune sand was

used for the fine aggregate and 19mm Greywacke stone was used for the coarse aggregate. The mix was designed to be slightly oversanded to reduce the inherent sample variability which might be influenced by the coarse aggregate distribution. The mix design is given in table 7.2 below.

Table 7.2: Mix design ($1m^3$).

w/c ratio	0.46
water (ℓ)	176
cement (kg) (OPC)	387
stone (kg)	966
sand (kg)	925

The concrete was mixed in a pan mixer for 2 minutes. The slump test was performed three times and measured to be 50, 70 and 55 mm. Care was taken to reduce the sampling error by remixing after every 5 cubes cast.

A total of 24 100 mm concrete cubes was cast. Of these 16 were used for the ruggedness tests (8 x 2 series)[1], 6 were used for compression tests and 2 extra were available if required.

The 16 cubes were wet cured for 7 days at 23°C (demoulded after 1 day, placed in curing tank for 6 days) and then placed in a controlled temperature and humidity room at 23°C and 60 % R.H. for 21 days. The remaining 6 cubes were wet cured for 28 days and crushed in an Amsler compression testing machine.

The 16 cubes were cored (68 mm diameter) perpendicular to the direction of casting. A set of three 25 mm discs was sliced from the core including 2 surface slices. The conductivity determinations of each set of 3 samples were averaged to obtain a test result.

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[1] The ruggedness test requires 2 series of tests.

7.2.3 Test results and calculations

Six cubes were randomly selected for compressive cube tests. The cube test results are displayed in table 7.3. The coefficient of variation of the cube tests was very low at 2.2 %. ie. the measures applied to reduce the sampling error appeared to have been successful.

Table 7.3: Cube strengths.

Compressive cube strengths at 28 days (MPa)						Mean (MPa)	C.V.
41.4	41.6	41.3	41.5	39.3	41.6	41.1	2.2 %

The ruggedness test results are displayed in table 7.4. A single test result consists of the mean of three conductivity determinations from three separate specimens from the same cube. The second test series is simply a repeat of the first and is required for statistical purposes.

Table 7.4: Ruggedness test results.

Test number	Test results (mS/cm)	
	1st series	2nd series
1	1.95	2.26
2	1.54	1.80
3	1.76	1.91
4	1.89	1.84
5	1.89	1.92
6	1.87	1.85
7	1.84	1.90
8	2.03	2.24
Mean	1.85	1.97

The statistical treatment of the data is shown in table 7.5. and the formulae used are addressed below the table.

Table 7.5: Calculations of test statistics (t) of the various factors.

Factor and level	First data set		Second data set		Difference between effects (d)	Mean effect	d^2	t
	Mean	Effect	Mean	Effect				
A. 4.5 M	1.908		1.978					
A. 5 M	1.784	0.124	1.953	0.025	0.099	0.074	0.0098	1.55
B. 25°C	1.880		1.973					
B. 22°C	1.812	0.068	1.958	0.016	0.052	0.042	0.0027	0.88
C. 5 M	1.834		1.933					
C. 1 M	1.858	0.025	1.998	0.066	0.041	0.045	0.0017	0.95
D. 14 days	1.852		1.881					
D. 7 days	1.839	0.013	2.050	0.169	0.182	0.078	0.0333	1.63
E. 5 hours	1.791		1.865					
E. 2 hours	1.901	0.110	2.066	0.201	0.091	0.155	0.0083	3.25
F. 22 hours	1.751		1.866					
F. 0 hours	1.940	0.189	2.065	0.199	0.010	0.194	0.0001	4.06
G. 0 min	1.804		1.968					
G. 2 min	1.888	0.084	1.963	0.006	0.090	0.039	0.0080	0.82
5 % critical t-value (d.f. = 7) = 2.36					$\bar{d}^2$ (variance of d, eqn. 7.4)		0.0091	
					s (standard deviation of single test result, see equation 7.3)		0.096	

The effect of each factor, such as A, was calculated as the absolute difference in the average of the measurements made at the two levels, for example:

$$Effect\ A = \left[\frac{\sum A(4.5)}{N/2} - \frac{\sum A(5)}{N/2}\right] \tag{7.1}$$

$$= \left[1.908 - 1.784\right]$$

$$= 0.124$$

where N was the number of measurements made (8 in this case).

The test statistic, t, was calculated as follows:

$$t_A = \frac{average\ effect\ A}{2s \div \sqrt{2N}} \tag{7.2}$$

where s is the standard deviation of a single test result (with N-1 degrees of freedom), and was obtained as follows:

$$s = \sqrt{\bar{d}^2} \tag{7.3}$$

where $\bar{d}^2$ is the variance of d, and d is the difference between the effects:

$$\bar{d}^2 \approx \sum d^2/(N-1) \tag{7.4}$$

The ruggedness test proposes the use of the 95 % significance level to make judgements. The critical t value at the 95 % siginificance level (d.f. = 7) is 2.36.

As an example, the test statistic for effect A was calculated below:

$$t_A = \frac{0.074}{2\sqrt{0.0091} \div \sqrt{2\times 8}}$$

$$= 1.55 \qquad (d.f. = 7)$$

$$< 2.36 \quad (5\ \%\ critical\ t\ value\ for\ d.f. = 7)$$

The calculated t value for effect A is not significant and therefore does not require tightening of the test method specification.

7.2.4 Discussion of results

The statistical t-values calculated for factors E (vacuum-saturation time) and F (soaking time)

exceeded the critical t value of 2.36 (3.25 and 4.06 respectively). This meant that the effects of changes in factors E and F were statistically significant at the 95 % significance level in terms of the inherent sample variation, and that tightening of test method specifications for these factors is required. The fact that the high and low levels of these factors differed substantially in the ruggedness tests (E: 2 - 5 hours and F: 0 - 18 hours) was most probably responsible for the higher t-values. The specifications chosen for these factors in the standard test method (see 7.3) were much more stringent (ie. E: 5 $\pm$ 0.5 hours and F: 18 $\pm$ 1 hours).

The t-values of the remaining factors (A, B, C, D and G) did not exceed the critical t-value of 2.36. These factors would therefore not require more stringent specifications on a statistical basis. For practical purposes however, closer limits were prescribed for most of these factors in the standard test method (7.3).

In conclusion, the chloride conduction test was found to be sufficiently rugged to withstand small changes in operating conditions likely to be found in different laboratories.

7.3 STANDARD TEST METHOD FOR THE CHLORIDE CONDUCTION TEST

What follows is a statement of the method required for carrying out the chloride conduction test in a standard way. It could therefore serve as a draft standard method, and is written in standard test format.

7.3.1 Scope

1) The chloride conduction test involves determining the DC conductivity of a concrete sample saturated with a sodium chloride solution. The test provides a rapid indication of the physical resistance of concrete to the penetration of chloride ions.
2) The values will be stated in mS/cm (milli Siemens per centimeter).

7.3.2 Referenced documents

1) Streicher, P.E. and Alexander, M.G., A chloride conduction test for concrete, *Cement and Concrete Research*, Vol. 25, No. 6, 1995, pp. 1284-1294.

2) ASTM C 1202-91, Standard test method for electrical indication of concrete's ability to resist chloride ion penetration.

7.3.3 Summary of test method

1) This test method consists of measuring the electrical current passed through 20 - 25 mm thick slices of 68 mm diameter cores. The specimens are saturated with a 5 M NaCl solution before the test. A potential difference of 2, 5 or 10 V dc is applied across the ends of the specimen, both of which are immersed in a sodium chloride solution. The conductivity is determined from the sample dimensions and the sample resistance ((area / thickness) x (potential difference / current)). One test result is calculated from the mean of three test determinations on the same material. The conductivity determination is linearly related to the steady state chloride diffusivity of the concrete by the diffusibility relationship. Note however that these properties are a function of the maturity of the concrete.

7.3.4 Significance and use

1) This test method is suitable for evaluation of materials and material proportions for design purposes as well as research and development purposes.
2) This test method is suitable for use as a quality control test on construction projects, provided suitable statistical criteria are used to make judgements.
3) The details of the test method apply to 20 - 25 mm x 68 mm diameter specimens. Other specimen thicknesses from 5 mm (mortar) to 40 mm may be used, but different conditioning times might be required.
4) Sample age may have significant effects on the test results, depending on the type of concrete and the curing procedure. Most concretes, if properly cured, become progressively and significantly less permeable with time.
5) Care should be taken in interpreting results of this test when it is used on surface treated concretes.

7.3.5 Interferences

1) Since the test results are a function of the electrical resistance of the specimen, the presence of reinforcing steel or other embedded electrically conductive materials may have a significant effect.

7.3.6 Apparatus

1) Oven capable of maintaining 50 °C ± 5 °C and a relative humidity below 20 %.

2) Vacuum saturation apparatus.

2.1) Vacuum pump - capable of maintaining 95 % vacuum in pressure vessel. A water vapour pumping rate of 0.045 kg/h will be required since the vacuum will be drawn over water.

2.2) Pressure vessel - approximately 25 l in volume, with a pressure gauge (accurate to 0.5 kPa) should be connected between the pump and the cylinder to maintain the vacuum when the pump is not running. The vessel also acts as a water trap since the vacuum will be drawn over water. Should a vessel not be used the pump oil should be changed after each operation.

2.3) Vacuum cylinder - approximately 4 l in volume and capable of withstanding vacuum pressures without imploding. The size of the cylinder will depend on the number of samples tested per run.

A transparent vacuum cylinder with an additional inlet valve is preferred to allow the saturating solution to be added after the specimens have been subjected to a vacuum. This will aid the process by removing the air from the concrete pores, thereby facilitating the flow of the solution into the concrete pores.

3) A water-cooled diamond tipped core barrel with an inner diameter of 68 mm, attached to a suitable coring drill.

4) A water-cooled moveable bed diamond saw (smooth blade).

5) Volumetric flask or container, a scale etc. to prepare the standard solutions.

6) Vernier caliper to measure specimen thickness.

7) Conduction cell - design shown in figure 7.1.

8) dc power source - 0-12 V, 0-1 A, stabilised.

9) Voltmeter and ammeter (2 multimeters) - digital 4 digit, 0-20 V range, 0-300 mA, rated accuracy 0.1 %.

10) Cable.

7.3.7 Reagents, materials and test cell

1) Sodium chloride solution - 5 M NaCl in tap water (impurities < 0.5 %).

Preparation of the sodium chloride solution:

A container marked at 10 l will be needed as well as 2.93 kg of CP grade NaCl (99 % purity). Add the salt to the container, and add distilled water but make sure not to exceed the 10 l level. Stir occasionally over a long period (1 day) until all the salt has dissolved. Heating the solution will speed the process, but allow the solution to cool again to avoid volumetric measurement errors. Top the container up to 10 l using distilled water only after all the salt has dissolved. The container should be sealed to prevent evaporation.

2) Saturated copper sulphate solution.

7.3.8 Test specimens

1) Coring and slicing - Usually samples such as 100 mm or 150 mm cubes or beams are specifically cast for the chloride conduction test. Standard attachments can then be used on the drill and the saw for the accurate positioning of the samples. Care must be taken to prevent damage to the samples such as corners breaking of. Discs should be of uniform thickness and have faces perpendicular to the cylinder axis. All discs should be between 20 and 25 mm in thickness. The best procedure for coring and slicing cubes is described below:

1.1) Coring - Ensure that the cube is placed at right angles to the coring barrel and securely fixed. Core the concrete cube to a depth of 30 mm.

1.2) Slicing - Ensure that the cube is placed at right angles to the slicing blade and securely fixed. Place the inside face of the blade at 22.5 mm. Slice the cube at a depth of 22.5 mm and remove the disc. It might be required to remove the as-cast surface of the specimen in which case the cube should first be sliced at 5 mm (outside face of blade) and then at 27.5 mm (inside face of blade). Both the coring and slicing operation must be done carefully and slowly to prevent damage to the samples.

2) Measure the thickness of the specimens using a vernier caliper. The thickness should ideally be measured at four equally spaced points around the edge of the specimen and averaged; alternatively the thickness at the middle of the specimen could be measured.

7.3.9 Conditioning

1) Oven drying - Place the discs in an oven at 50 °C and < 20 % RH for 7 days + 2 days. Before vacuum saturation, the samples are left to cool in a dry environment (RH < 60 %) for an hour at room temperature.

2) Vacuum saturation - Before the chloride conduction test the samples are vacuum saturated in the 5 M NaCl solution for 5 hours, and left to soak for an additional 18 ± 1 hours before the test. Two methods are described below. Method 2 is preferred as it reduces the problem of water contaminating the pump oil. Method 2 requires a transparent vacuum cylinder and an additional inlet to allow the addition of the saturating solution under vacuum.

3) Method 1

   3.1) Place the samples in the cylinder and add some of the 5 M NaCl solution until all the samples are completely immersed.

   3.2) Connect the vacuum pump to the pressure vessel, and the vessel to the cylinder, and apply a vacuum. A vacuum of between 90 and 80 % will be needed for 5 hours. The pump need only run occasionally to keep the vacuum above 80 %.

   3.3) Leave the samples immersed in the solution for an additional 18 ± 1 hours before the test.

4) Method 2

   4.1) Place the samples in the dry cylinder.

   4.2) Connect the vacuum pump to the pressure vessel, and the vessel to the cylinder, and apply a vacuum. A vacuum of above 95 % will be needed for 3 hours.

   4.3) While maintaining the vacuum pressure, add some of the 5 M NaCl solution until all the samples are completely immersed (a transparent cylinder is required). Keep the vacuum between 90 and 80 % for an additional 5 hours.

   4.4) Leave the samples immersed in the solution for an additional 18 ± 1 hours before the test.

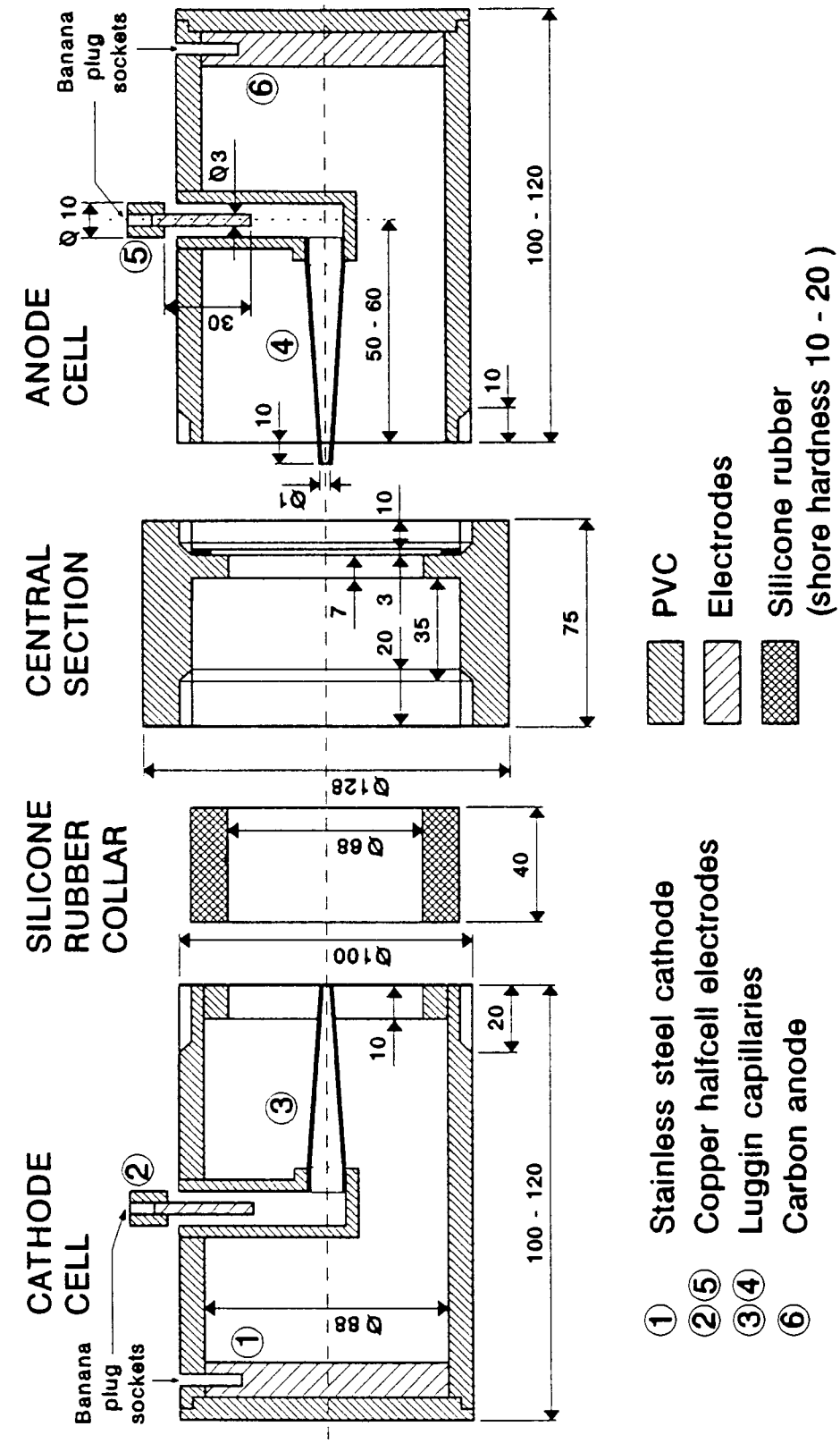

Figure 7.1: Design of the chloride conduction cell.

7.3.10 Chloride conduction test

1) The chloride conduction test must either be done in a controlled temperature room at 25 °C ± 0.5 °C, or alternatively other measures must be taken to ensure that the solutions used as well as the saturated samples are at this temperature when tested.

2) Fill both cells with the 5 M NaCl solution (see figure 7.2).

3) Take the specimen from the saturating solution, and place it in the centre of the silicon rubber collar inside the central section of the apparatus.

4) Screw the central section onto the cathode cell, thereby clamping the specimen by the lateral Poisson's expansion of the silicon collar. Screw the cathode/central section unit onto the anode cell.

5) Ensure that the halfcell tubes are filled with the saturated copper sulphate solution and that the halfcell electrodes are clean.

6) Arrange the circuit as shown in figure 7.3 with both the ammeter and voltmeter connected. Measure the current at the applied voltage. Generally 10 V is used, but 5 or 2 V can be used for very permeable or thin samples in order not to exceed the reading limits of the ammeter.

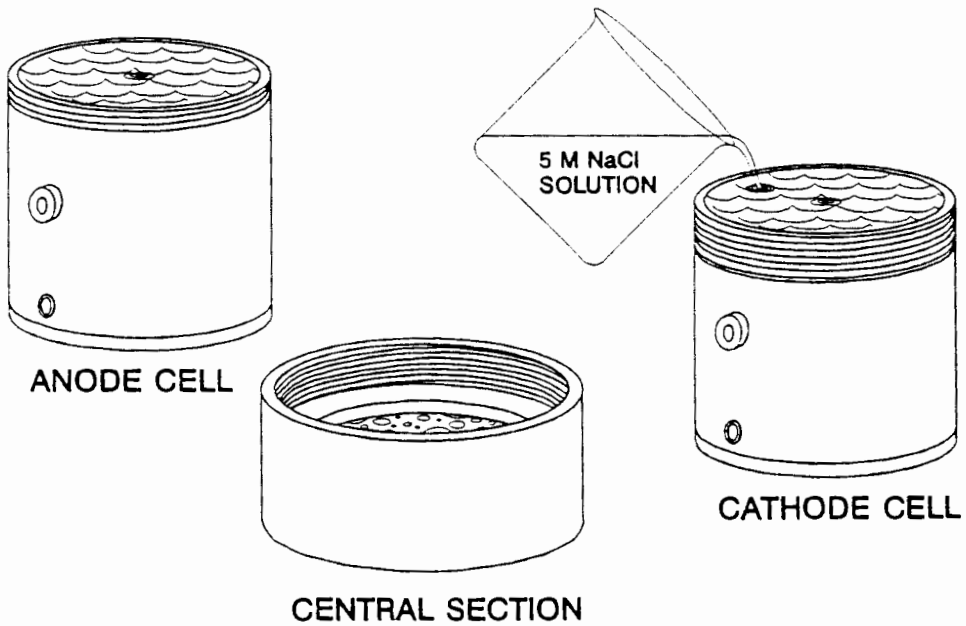

Figure 7.2: Filling of cells with salt solution.

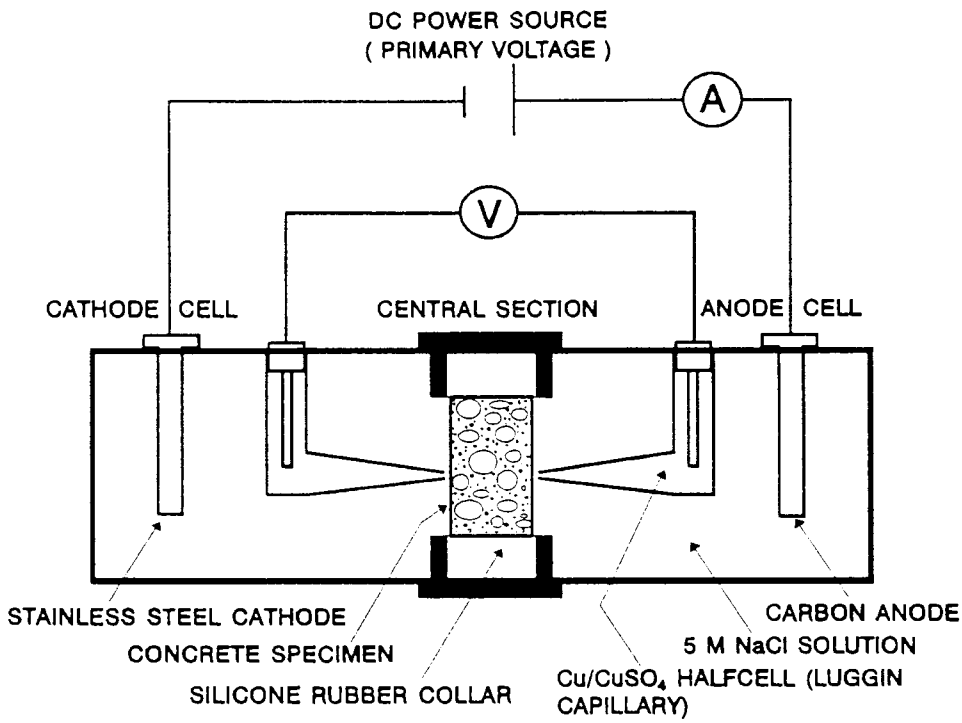

Figure 7.3: Schematic representation of test arrangement.

7.3.11 Calculation of results

1) To determine the conductivity of each specimen, the measured current, potential difference across specimen and the specimen dimensions are substituted in equation 7.5:

$$\sigma = \frac{i}{V}\,\frac{t}{A} \qquad (7.5)$$

where σ ... conductivity of sample [mS/cm]

i ... electric current [mA]

V ... potential difference [V]

t ... thickness of specimen [cm]

A ... cross-sectional area of specimen [cm^2]

2) Three test determinations are averaged to obtain one test result. Six test determinations can also be used where a higher precision is required.

7.3.12 Report

1) Report the following if known (ref. 7.3.2 no. 2):
   1.1) Source of specimen (or core),
   1.2) Identification number of specimen (and core),
   1.3) Location of specimen within core or cylinder,
   1.4) Type of concrete, including binder type, water/cement ratio, and other relevant data supplied with specimens,
   1.5) Description of specimen,
   1.6) Curing history of specimen,
   1.7) Unusual specimen preparation, for example, removal of surface treatment,
   1.8) Test results.

7.3.13 Precision and bias - This work is still in progress

1) Bias - The procedure of this test method for measuring the resistance of concrete to chloride ion penetration has no bias because the value of this resistance can be defined only in terms of a test method.

7.4 PRECISION STATEMENTS

When a specific property of concrete is tested, the test determinations will exhibit a degree of variability (Popovics, 1982, p.15). The portion of variability caused by the testing itself is characterised by precision indexes such as "repeatability" or "reproducibility" (ASTM C 670, 1991; ASTM C 802-87, 1991). These precision indexes may be used as guides to determine with a prescribed degree of certainty whether a given series of results can be considered valid under the conditions assumed in the test method, whether an operator is qualified to perform the test in question, and whether a laboratory is qualified to perform the test in question.

Ideally, an interlaboratory test programme (such as ASTM C802-87) is required to determine the precision of a test method. Such a programme requires a number of participating laboratories (ideally 12) with personnel experienced with the test method. At the time of completing this thesis, the test was not sufficiently widely used to allow the implementation

of an interlaboratory test programme. However, an attempt was made to meet most of the criteria required for an interlaboratory study. The criteria that have been met are listed below:

1) The existence of a valid and well-written test method developed in a competent laboratory which has been subjected to a ruggedness test (allowing a proper degree of control over conditions affecting the test).
2) Appropriately designed apparatus for the test.
3) The existence of knowledge about how changes in materials affect the test result.

An attempt was made to estimate precision indexes for the test based on work done in our laboratory (see section 7.4.3). Before dealing with this, common precision statement and measurement terminology are defined.

7.4.1 Precision statement terminology (ASTM C670-91a)

1. One-sigma limit (1s) is the estimate of the standard deviation characteristic of the total statistical population. It is the indication of the variability of a large group of individual test results obtained under similar conditions.
2. One-sigma limit in percent (1s%) is the estimate of the coefficient of variation of the population. It is often used when the standard deviation is essentially proportional to the average for different levels of the property in question (that is, the coefficient of variation is essentially constant).
3. Difference two-sigma limit (d2s) (or in percent - d2s%) is the acceptable difference between two test results.
4. Single-operator one-sigma limit (repeatability) is a quantitative estimate of the variability of a large group of individual test results when the tests have been made on the same material by a single operator using the same apparatus in the same laboratory over a relatively short period of time.
5. Multilaboratory one-sigma limit (reproducibility) is a quantitative estimate of the variability of a large group of individual test results when each test has been made in a different laboratory and every effort has been made to make the test portions of the material as nearly identical as possible.

7.4.2 Measurement terminology (ASTM E177-90a)

A quantitative test method may have three distinct stages:
(1) the direct measurement or **observation** of dimensions or properties; (2) the arithmetical combination of the observed values to obtain a single **determination**; and (3) the arithmetical combination of a number of determinations to obtain the **test result** of the test method.

7.4.3 Statistical analysis of the series 2 test data

The series 2 tests involved the testing of a wide range of concrete mixes using two different operators in one laboratory. The concrete specimens were derived from three batches and surface specimens were tested, which most probably increased the variability (see section 7.4.4). A statistical analysis of the data was performed to obtain an estimate of precision indexes for the test.

In the project three test determinations were combined to yield one test result. Precision indexes were estimated from the variation within each set of three test determinations. The variation within each data set was characterised by the standard deviation, s, or the coefficient of variation, cv. Table 7.6 shows the series 2 chloride conductivity test results, standard deviations and coefficients of variation in ascending order of chloride conductivity. Table 7.7 shows the same values, but in chronological order.

Due to the small sample size (3), there was a great deal of variation between the individual s and cv values. Twenty-one of these values were therefore combined for analysis purposes. The number '21' is arbitrary, and was chosen to eliminate sufficient noise without losing too much detail. A squared average was calculated, which is the statistically correct way of calculating a combined s or cv (ASTM E 178-80). The procedure is described in detail:

Calculating a running average of cv and s using 21 values of cv in each case:

Data:

cv values: cv_1, cv_2, cv_3, ... cv_n (column 4, table 7.6, 7.7).

$\bar{x}$ values: $\bar{x}_1$, $\bar{x}_2$, $\bar{x}_3$, ... $\bar{x}_n$ (column 2, table 7.6, 7.7).

$$\bar{cv}_{i,\,21} = \sqrt{\frac{\sum_{j=i-10}^{i+10} cv_j^2}{21}} \qquad (7.6)$$

$$\bar{s}_{i,\,21} = \frac{\bar{cv}_{i,\,21} \times \bar{x}_i}{100\ \%}$$

Table 7.6: Statistical analysis of the series 2 test data (order of ascending chloride conductivity).

(1) Mix no. / wet curing (days)	(2) Chloride conductivity result (mS/cm)	(3) Standard deviation (mS/cm)	(4) Coefficient of variation (%)	(5) Squared coefficient of variation	(6) Running ave. (21 values) coefficient of variation (%)	(7) Running average (21 values) stand. deviation (mS/cm)
21/7	0.11	0.008	7.01%	0.004916		
36/28	0.17	0.012	7.35%	0.005398		
36/7	0.18	0.007	4.01%	0.001604		
24/28	0.20	0.012	5.87%	0.003447		
21/1	0.22	0.010	4.45%	0.001983		
35/28	0.28	0.007	2.46%	0.000603		
35/7	0.30	0.053	17.89%	0.032014		
27/28	0.32	0.027	8.47%	0.007181		
29/28	0.34	0.036	10.75%	0.011551		
29/7	0.39	0.029	7.44%	0.005540		
27/7	0.40	0.050	12.72%	0.016181	0.124	0.049
26/28	0.44	0.058	13.21%	0.017458	0.125	0.055
18/28	0.44	0.118	26.58%	0.070667	0.125	0.055
18/7	0.46	0.029	6.21%	0.003852	0.124	0.058
24/7	0.54	0.099	18.33%	0.033608	0.126	0.068
36/1	0.57	0.082	14.43%	0.020813	0.134	0.076
20/28	0.61	0.038	6.29%	0.003958	0.137	0.083
17/28	0.70	0.092	13.17%	0.017354	0.134	0.094
17/7	0.73	0.058	7.95%	0.006316	0.133	0.097
18/1	0.76	0.163	21.33%	0.045509	0.133	0.102
20/7	0.80	0.097	12.18%	0.014839	0.142	0.113
28/28	0.82	0.064	7.80%	0.006083	0.141	0.116
23/28	0.85	0.062	7.35%	0.005398	0.139	0.119
17/1	0.88	0.026	2.91%	0.000847	0.128	0.112
19/28	0.91	0.094	10.38%	0.010776	0.128	0.116
26/7	0.92	0.195	21.32%	0.045452	0.122	0.112
27/1	1.02	0.141	13.79%	0.019025	0.119	0.121
7/28	1.07	0.118	11.06%	0.012242	0.119	0.127
24/1	1.09	0.057	5.19%	0.002693	0.119	0.129
7/1	1.15	0.140	12.21%	0.014904	0.118	0.136
29/1	1.15	0.277	24.04%	0.057796	0.109	0.126
25/28	1.22	0.091	7.42%	0.005502	0.106	0.130
7/7	1.26	0.132	10.46%	0.010948	0.107	0.135
11/28	1.31	0.108	8.26%	0.006816	0.111	0.145
30/7	1.31	0.077	5.87%	0.003447	0.112	0.147
15/7	1.39	0.052	3.72%	0.001380	0.111	0.155
30/28	1.40	0.090	6.39%	0.004079	0.105	0.148
23/7	1.43	0.101	7.10%	0.005037	0.103	0.148
28/7	1.46	0.189	12.98%	0.016852	0.101	0.147
15/28	1.48	0.105	7.08%	0.005017	0.103	0.151
11/7	1.51	0.070	4.60%	0.002118	0.101	0.153
15/1	1.54	0.043	2.80%	0.000787	0.089	0.137
25/7	1.61	0.168	10.46%	0.010937	0.088	0.141
26/1	1.68	0.247	14.70%	0.021600	0.098	0.165
11/1	1.76	0.147	8.33%	0.006935	0.098	0.173
2/28	1.92	0.162	8.45%	0.007148	0.100	0.191
19/7	1.92	0.260	13.57%	0.018406	0.100	0.191
3/7	2.03	0.193	9.51%	0.009048	0.101	0.205
2/7	2.05	0.077	3.77%	0.001422	0.103	0.211
30/1	2.06	0.213	10.34%	0.010700	0.099	0.204
6/28	2.06	0.196	9.52%	0.009067	0.100	0.205
32/7	2.12	0.206	9.74%	0.009490	0.099	0.211
14/7	2.12	0.059	2.81%	0.000787	0.101	0.214
20/1	2.16	0.495	22.89%	0.052382	0.106	0.229
3/28	2.17	0.165	7.63%	0.005826	0.113	0.244
32/28	2.18	0.219	10.07%	0.010132	0.115	0.249
22/28	2.18	0.073	3.34%	0.001116	0.114	0.249
35/1	2.19	0.215	9.83%	0.009671	0.115	0.251
14/28	2.20	0.239	10.88%	0.011837	0.113	0.249
16/28	2.21	0.106	4.79%	0.002291	0.113	0.250
6/7	2.21	0.183	8.27%	0.006842	0.111	0.246
9/28	2.21	0.079	3.58%	0.001283	0.110	0.243
13/28	2.22	0.197	8.89%	0.007897	0.108	0.240

Table 7.6 - continued

(1) Mix no. / wet curing (days)	(2) Chloride conductivity result (mS/cm)	(3) Standard deviation (mS/cm)	(4) Coefficient of variation (%)	(5) Squared coefficient of variation	(6) Running ave. (21 values) coefficient of variation (%)	(7) Running average (21 values) stand. deviation (mS/cm)
10/28	2.29	0.405	17.67%	0.031221	0.108	0.249
5/28	2.30	0.531	23.04%	0.053076	0.109	0.250
6/1	2.35	0.296	12.60%	0.015873	0.109	0.257
9/7	2.38	0.140	5.87%	0.003447	0.119	0.284
5/1	2.42	0.374	15.47%	0.023941	0.119	0.288
13/1	2.42	0.093	3.84%	0.001477	0.119	0.287
16/7	2.42	0.110	4.53%	0.002054	0.117	0.284
1/28	2.43	0.080	3.28%	0.001077	0.117	0.284
13/7	2.46	0.110	4.47%	0.002001	0.117	0.287
10/1	2.52	0.105	4.16%	0.001729	0.117	0.294
23/1	2.56	0.095	3.73%	0.001389	0.119	0.304
2/1	2.61	0.604	23.11%	0.053426	0.114	0.298
5/7	2.62	0.250	9.54%	0.009102	0.109	0.285
10/7	2.68	0.647	24.15%	0.058303	0.110	0.295
14/1	2.71	0.056	2.07%	0.000427	0.112	0.304
1/7	2.71	0.228	8.39%	0.007045	0.107	0.291
32/1	2.73	0.184	6.74%	0.004544	0.110	0.299
22/7	2.76	0.084	3.04%	0.000925	0.109	0.302
1/1	2.80	0.220	7.86%	0.006178	0.116	0.325
22/1	2.88	0.127	4.40%	0.001940	0.116	0.335
9/1	2.95	0.391	13.28%	0.017636	0.124	0.366
28/1	3.01	0.269	8.93%	0.007979	0.124	0.375
3/1	3.26	0.543	16.63%	0.027664	0.114	0.371
4/28	3.44	0.504	14.65%	0.021459	0.113	0.389
25/1	3.48	0.416	11.95%	0.014277		
12/28	3.59	0.127	3.53%	0.001248		
8/7	3.64	0.396	10.89%	0.011853		
12/7	3.77	0.139	3.68%	0.001357		
8/28	4.15	0.743	17.91%	0.032077		
12/1	4.34	0.280	6.45%	0.004160		
8/1	4.36	0.893	20.50%	0.042037		
4/7	4.59	0.130	2.83%	0.000803		
19/1	4.65	0.050	1.08%	0.000117		
16/1	4.66	0.360	7.74%	0.005986		

Table 7.7: Statistical analysis of the series 2 test data (chronological order).

(1) Mix no. / wet curing (days)	(2) Chloride conductivity result (mS/cm)	(3) Standard deviation (mS/cm)	(4) Coefficient of variation (%)	(5) Squared coefficient of variation	(6) Running average coefficient of variation (%)
1/1	2.80	0.220	7.86%	0.006178	
1/7	2.71	0.228	8.39%	0.007045	
1/28	2.43	0.080	3.28%	0.001077	
2/1	2.61	0.604	23.11%	0.053426	
2/7	2.05	0.077	3.77%	0.001422	
2/28	1.92	0.162	8.45%	0.007148	
3/1	3.26	0.543	16.63%	0.027664	
3/7	2.03	0.193	9.51%	0.009048	
3/28	2.17	0.165	7.63%	0.005826	
4/1	7.69	2.544	33.10%	0.109532	
4/7	4.59	0.130	2.83%	0.000803	13.92%
4/28	3.44	0.504	14.65%	0.021459	14.52%
5/1	3.42	0.374	15.47%	0.023941	14.59%
5/7	2.62	0.250	9.54%	0.009102	15.09%
5/28	2.30	0.531	23.04%	0.053076	14.52%
6/1	2.35	0.296	12.60%	0.015873	14.55%
6/7	2.21	0.183	8.27%	0.006842	14.45%
6/28	2.06	0.196	9.52%	0.009067	14.02%
7/1	1.15	0.140	12.21%	0.014904	14.83%
7/7	1.26	0.132	10.46%	0.010948	15.23%

Table 7.7 - continued

(1) Mix no. / wet curing (days)	(2) Chloride conductivity result (mS/cm)	(3) Standard deviation (mS/cm)	(4) Coefficient of variation (%)	(5) Squared coefficient of variation	(6) Running average coefficient of variation (%)
7/28	1.07	0.118	11.06%	0.012242	13.54%
8/1	4.36	0.893	20.50%	0.042037	13.56%
8/7	3.64	0.396	10.89%	0.011853	13.30%
8/28	4.15	0.743	17.91%	0.032077	12.94%
9/1	2.95	0.391	13.28%	0.017636	12.80%
9/7	2.38	0.140	5.87%	0.003447	11.79%
9/28	2.21	0.079	3.58%	0.001283	11.50%
10/1	2.52	0.105	4.16%	0.001729	11.40%
10/7	2.68	0.647	24.15%	0.058303	11.37%
10/28	2.29	0.405	17.67%	0.031221	11.07%
11/1	1.76	0.147	8.33%	0.006935	10.85%
11/7	1.51	0.070	4.60%	0.002118	10.84%
11/28	1.31	0.108	8.26%	0.006816	9.89%
12/1	4.34	0.280	6.45%	0.004160	9.63%
12/7	3.77	0.139	3.68%	0.001357	8.94%
12/28	3.59	0.127	3.53%	0.001248	8.62%
13/1	2.42	0.093	3.84%	0.001477	8.59%
13/7	2.46	0.110	4.47%	0.002001	8.61%
13/28	2.22	0.197	8.89%	0.007897	8.59%
14/1	2.71	0.056	2.07%	0.000427	7.00%
14/7	2.12	0.059	2.81%	0.000787	6.51%
14/28	2.20	0.239	10.88%	0.011837	7.80%
15/1	1.54	0.043	2.80%	0.000787	7.85%
15/7	1.39	0.052	3.72%	0.001380	9.59%
15/28	1.48	0.105	7.08%	0.005017	9.49%
16/1	4.66	0.360	7.74%	0.005986	9.91%
16/7	2.42	0.110	4.53%	0.002054	10.14%
16/28	2.21	0.106	4.79%	0.002291	11.27%
17/1	0.88	0.026	2.91%	0.000847	11.54%
17/7	0.73	0.058	7.95%	0.006316	11.46%
17/28	0.70	0.092	13.17%	0.017354	11.49%
18/1	0.76	0.163	21.33%	0.045509	11.57%
18/7	0.46	0.029	6.21%	0.003852	11.37%
18/28	0.44	0.118	26.58%	0.070667	11.37%
19/1	4.65	0.050	1.08%	0.000117	11.37%
19/7	1.92	0.260	13.57%	0.018406	11.29%
19/28	0.91	0.094	10.38%	0.010776	11.27%
20/1	2.16	0.495	22.89%	0.052382	11.34%
20/7	0.80	0.097	12.18%	0.014839	11.35%
20/28	0.61	0.038	6.29%	0.003958	12.02%
21/1	0.22	0.010	4.45%	0.001983	11.96%
21/28	0.11	0.008	7.01%	0.004916	11.90%
22/1	2.88	0.127	4.40%	0.001940	11.18%
22/7	2.76	0.084	3.04%	0.000925	11.22%
22/28	2.18	0.073	3.34%	0.001116	10.12%
23/1	2.56	0.095	3.73%	0.001389	11.14%
23/7	1.43	0.101	7.10%	0.005037	11.12%
23/28	0.85	0.062	7.35%	0.005398	11.29%
24/1	1.09	0.057	5.19%	0.002693	10.50%
24/7	0.54	0.099	18.33%	0.033608	10.33%
24/28	0.20	0.012	5.87%	0.003447	10.42%
25/1	3.48	0.416	11.95%	0.014277	10.76%
25/7	1.61	0.168	10.46%	0.010937	10.78%
25/28	1.22	0.091	7.42%	0.005502	11.95%
26/1	1.68	0.247	14.70%	0.021600	12.04%
26/7	0.92	0.195	21.32%	0.045452	12.25%
26/28	0.44	0.058	13.21%	0.017458	12.43%
27/1	1.02	0.141	13.79%	0.019025	12.40%
27/7	0.40	0.050	12.72%	0.016181	12.37%
27/28	0.32	0.027	8.47%	0.007181	12.41%
28/1	3.01	0.269	8.93%	0.007979	11.93%
28/7	1.46	0.189	12.98%	0.016852	12.07%
28/28	0.82	0.064	7.80%	0.006083	11.98%
29/1	1.15	0.277	24.04%	0.057796	12.39%
29/7	0.39	0.029	7.44%	0.005540	12.29%
29/28	0.34	0.036	10.75%	0.011551	12.28%

Table 7.7 - continued

(1) Mix no. / wet curing (days)	(2) Chloride conductivity result (mS/cm)	(3) Standard deviation (mS/cm)	(4) Coefficient of variation (%)	(5) Squared coefficient of variation	(6) Running average coefficient of variation (%)
30/1	2.06	0.213	10.34%	0.010700	11.40%
30/7	1.31	0.077	5.87%	0.003447	11.14%
30/28	1.40	0.090	6.39%	0.004079	
32/1	2.73	0.184	6.74%	0.004544	
32/7	2.12	0.206	9.74%	0.009490	
32/28	2.18	0.219	10.07%	0.010132	
35/1	2.19	0.215	9.83%	0.009671	
35/7	0.30	0.053	17.89%	0.032014	
35/28	0.28	0.007	2.46%	0.000603	
36/1	0.57	0.082	14.43%	0.020813	
36/7	0.18	0.007	4.01%	0.001604	
36/28	0.17	0.012	7.35%	0.005398	

The running average standard deviation is plotted against chloride conductivity in figure 7.4. It can be seen that the standard deviation is essentially proportional to the average for the different levels of the property measured (ie. the coefficient of variation is essentially constant). This meant that precision indexes based on the coefficient of variation (1s%, d2s%) would be more suitable for the chloride conduction test.

The running average coefficient of variation was plotted againts mix number (chronological order) in figure 7.5. Note that a different operator was used after mix 11, and the test method was only finalised at this stage. It can be seen that the coefficient of variation was slightly lower after mix 11 which is most probably as a result of the new operator and small changes in the test method. The coefficient of variation also seems a bit higher from mix 25 onwards. Mixes 25 - 29 and 33 - 36 were slag mixes which indicates the possibility that cement type affects variability.

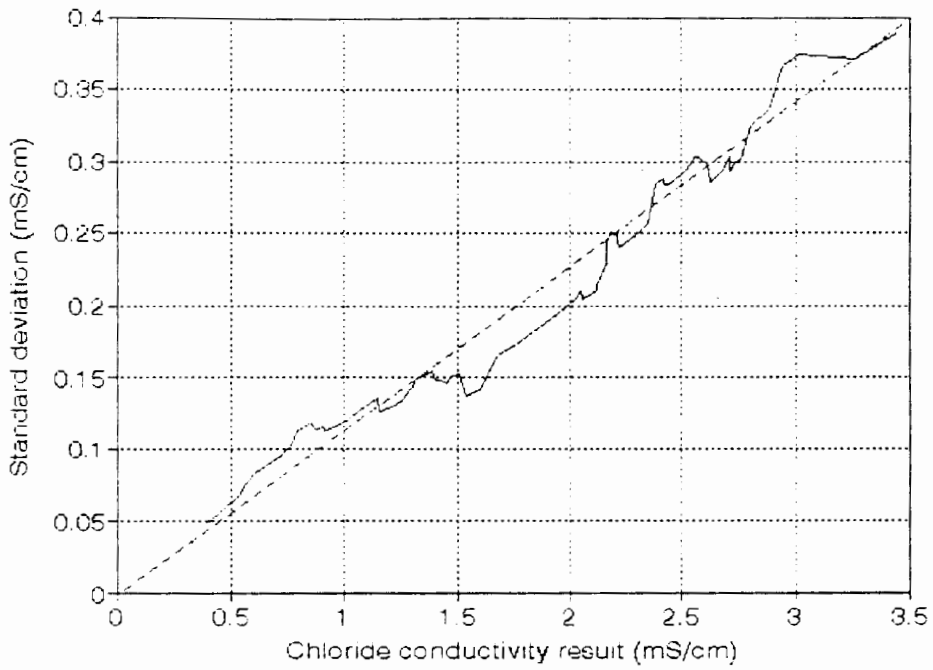

Figure 7.4: Running average standard deviation versus chloride conductivity result.

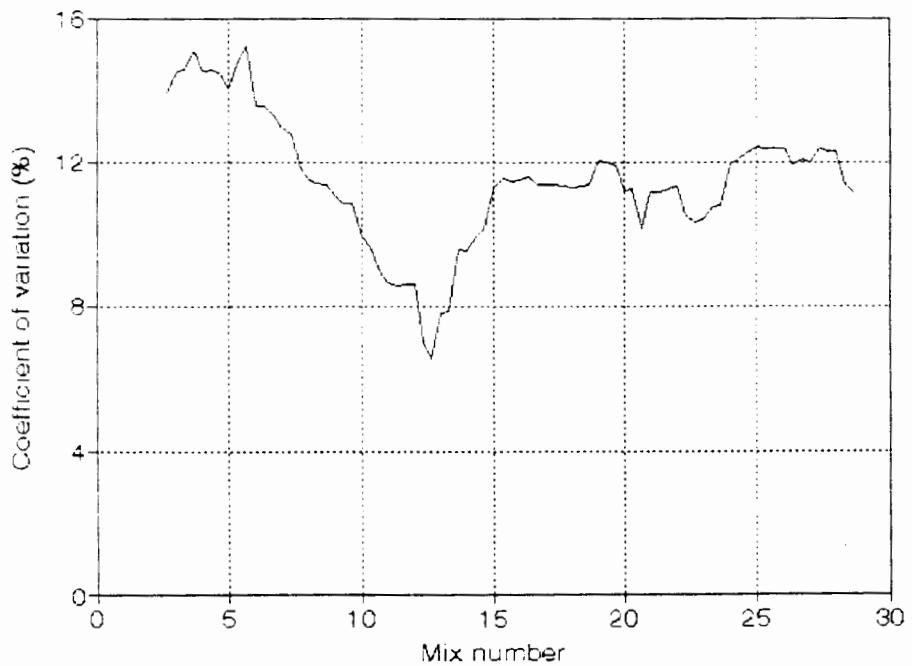

Figure 7.5: Running average coefficient of variation versus mix number (ie. chronological order). Note: Operator changed after mix 11.

The combined coefficient of variation from mix 12 to 36 was calculated as 10.6 %. To determine the single-operator coefficient of variation (1s%) of the chloride conduction test involves dividing this number by the square root of the number of test determinations included in a test result (see table 7.8).

In the series 2 tests, 3 test determinations were combined to obtain one test result which meant the coefficient of variation of the test was 6.1 %.

Table 7.8: Estimated single-operator coefficient of variation (1s%) of the chloride conductivity test (series 2 test data).

Number of test determinations included in test result	1	2	3	4	5	6
1s%	10.6%	7.5%	6.1%	5.3%	4.7%	4.3%

7.4.4 Statistical analysis of thickness tests (chapter 6)

The thickness tests were conducted on 15 - 30 mm thick 50 MPa OPC concrete specimens. The specimens were all derived from one concrete batch and the as-cast surfaces of the specimens were removed. A significantly lower single-operator coefficient of variation was calculated (see table 7.9) relative to the series 2 test results. The values in table 7.9 are based on the 1 day results of the 20 mm and 25 mm specimens (9 degrees of freedom).

Table 7.9: Estimated single-operator coefficient of variation (1s%) of the chloride conductivity test (thickness tests).

Number of test determinations included in test result	1	2	3	4	5	6
1s%	6.3%	4.5%	3.6%	3.1%	2.8%	2.6%

The lower 1s% was ascribed to the fact that one batch was used and the as-cast concrete surfaces removed. The results do not carry as much weight as the series 2 test results since

they involve only one mix. However, it is an indication of the possible precision that can be achieved.

7.4.5 Acceptable differences between test results and test determinations

The precision indexes can be used to determine whether two test results differ significantly, and whether the range of a set of test determinations is acceptable.

The acceptable difference between two test results (2ds%) is approximately equal to 1s% x 2.8 at the 95 % significance level (ASTM C670-91a). Two results which differ by more than this are statistically significantly different.

The acceptable range of test determinations (with respect to the average result) on the same material is shown in table 7.10.

Table 7.10: Acceptable range of test determinations (ASTM C670-91a).

Number of test determinations averaged to obtain a test result	Multiplier of 1s% for averages to obtain maximum acceptable range of individual test determinations at the 95 % level
3	5.7
4	7.3
5	8.6
6	9.9

7.5 CONCLUSIONS

A ruggedness test was used to determine to what degree the conditions specified in the test method must be controlled. In general the chloride conduction test was found to be sufficiently rugged to withstand small changes in operating conditions found in different laboratories.

Based on the trial work (chapter 6) and the ruggedness test conducted, a standard test method for the chloride conduction test was written, and a detailed design of the test apparatus was prepared.

At the time of completing this thesis, the test was not sufficiently widely used to allow the implementation of an interlaboratory test programme. However, an attempt was made to meet most of the criteria required for an interlaboratory study.

Data from the series 2 tests was used to estimate the precision of the chloride conduction test. The single-operator coefficient of variation of the test (1s%) was estimated to be 6.1 % when a test result constitutes 3 test determinations, and 4.3 % when a test result constitutes 6 test determinations. The data included between batch variability and the as-cast concrete surfaces were not removed. A lower coefficient of variation is likely should between batch variability be excluded, and the as-cast concrete surfaces discarded.

7.6 REFERENCES

ASTM C 670-91a, Standard practice for preparing precision and bias statements for test methods for construction materials, 1991.

ASTM C 802-87, Standard practice for conducting an interlaboratory test program to determine the precision of test methods for construction materials.

ASTM C 1202-91, Standard test method for electrical indication of concrete's ability to resist chloride ion penetration.

ASTM E 177-90a, Standard practice for use of the terms precision and bias in ASTM test methods.

ASTM E 178-80, Standard practice for dealing with outlying observations.

ASTM E 1169-89, Standard guide for conducting ruggedness tests.

CHAPTER 8

CORRELATIONS BETWEEN CHLORIDE CONDUCTIVITY TEST RESULTS AND IN-SITU CHLORIDE INGRESS

8.1 INTRODUCTION

Durability index tests generally focus on specific material properties at a specific time (usually early age), while the process of degradation in-situ involves a number of mechanisms over a protracted period of time. Direct relationships between a single durability index test result (at a specific time) and in-situ performance parameters (over a range of time) are therefore likely to be tenuous.

Predicting long-term durability performance from early-age durability index test results would therefore require a suitable durability model taking account of all the relevant factors. The process of developing such a model would require correlation studies between laboratory index test values and in-situ performance parameters.

This chapter commences with a study of existing chloride ingress formulae to provide insight into the roles of the various factors involved in chloride ingress. The factors consist of the physical and the chemical resistance of concrete to chloride ingress, the changes in concrete properties with time and the influence of the environment. Correlation studies from the series 1 and 2 tests are then discussed. The correlation studies are at an early stage and are therefore not sufficient for the full development of a chloride ingress model.

In the series 1 tests, chloride index values from the modified Dundee chloride test were correlated with 2 year chloride ingress results. Although this work does not involve the chloride conductivity test, it provides useful information on the variability of in-situ chloride ingress parameters and the use of alternative chloride ingress parameters.

8.2 BACKGROUND: CHLORIDE INGRESS FORMULAE

Concrete is a porous material, and all externally derived deleterious substances enter concrete through the pore space. The rate at which these substances move through the pore structure largely determines the rate at which degradation proceeds.

Chloride corrosion of steel is a typical example of this where chloride ions enter concrete and initiate corrosion of the reinforcement once a critical chloride level is exceeded at the steel. There is therefore great interest in predicting chloride levels in concrete.

The rate of chloride ingress depends both on the physical pore structure, as well as chemical properties of the concrete, since concrete can bind a portion of the chloride ions which enter.

Most formulae that predict chloride ingress assume that diffusion is the main transport mechanism, and characterise the physical pore structure of concrete in terms of a chloride diffusion coefficient. Some include the effect of binding in this coefficient, and others take account of binding explicitly. Simplifying assumptions are often made so that linear solutions can be obtained. These formulae are useful in understanding the processes involved, but they are often not able to describe the general conditions on site.

It is important to distinguish between the various chloride diffusion coefficients that have been defined, and to realise that all these coefficients are not fundamental material properties as they are influenced by a number of factors, and they change with time.

8.2.1 Fick's second law

The most widely used formula for predicting chloride levels in concrete is derived from Fick's second law for non-steady state diffusion. The change in concentration ($\partial c_m/\partial t$) will be affected by chloride binding and not just diffusion, and hence the equation yields an apparent diffusivity D_a. Fick's second law states that for unidirectional diffusion,

$$\frac{\partial c_m}{\partial t} = D_a \frac{\partial^2 c_m}{\partial x^2} \qquad (8.1)$$

where c_m ... chloride concentration in the medium
t ... time
x ... depth into the medium
D_a ... apparent diffusion coefficient

The analytical integration of this equation is simply obtained under the following assumptions

(Crank, 1975):

1. The medium is homogeneous and does not change with time, ie. D is constant in space and time.
2. The medium is semi-infinite, and exposed to a solution on the one side with a constant chloride concentration; the surface chloride level converges to that constant value after a short period of time,

$$c_m = 0 \quad at \quad t = 0 \quad and \quad 0 < x < \infty$$
$$c_m = C_s \quad at \quad x = 0 \quad and \quad 0 < t < \infty \qquad (8.2)$$

where c_x ... chloride concentration at depth x
C_s ... surface chloride concentration

Solving the partial differential equation for these boundary conditions yields,

$$C_{x,t} = C_s[1 - erf(\frac{x}{2\sqrt{D_a t}})] \qquad (8.3)$$

where erf ... error function
$C_{x,t}$ ... chloride concentration at depth x at time t

By dividing both sides by C_s, the equation becomes dimensionless since $C_{x,t}$ and C_s have the same units. Usually the values of $C_{x,t}$ and C_s are stated in terms of percentage total or water soluble chloride contents w.r.t. cement content since critical chloride levels are usually stated in these units. The units of the remaining terms x, D and t should be such that the term $x/2\sqrt{(Dt)}$ is dimensionless eg. cm, cm^2/s and s, respectively.

If an initial level of chlorides, C_0, is present in the concrete the equation becomes

$$C_{x,t} - C_0 = [C_s - C_0] [1 - erf(\frac{x}{2\sqrt{D_a t}})]$$
$$or \quad C_{x,t} = C_s [1 - erf(\frac{x}{2\sqrt{D_a t}})] \qquad (8.4)$$
$$where \; C = C - C_0$$

(Miyagawa, 1991)

The initial chloride content is subtracted from both the surface chloride content and the internal chloride content (see figure 8.1).

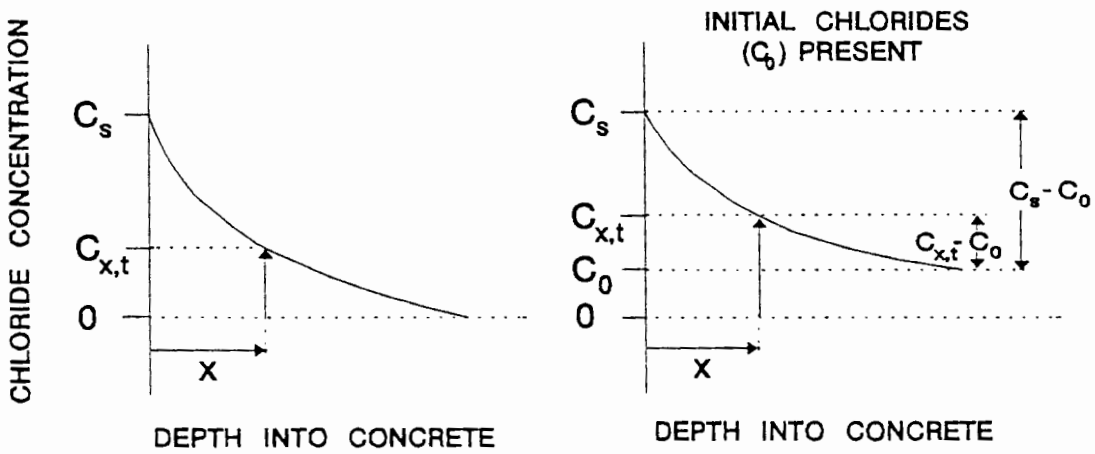

Figure 8.1: Chloride profile through concrete.

8.2.1.1 Surface chloride levels

The assumption that the surface chloride level reaches a constant value in a short period of time is not always valid since concretes exposed to evaporation processes could have surface chloride levels increasing with time. The accuracy of surface chloride estimates at early ages (0.5 - 3 years) is generally poor due to the steepness of the chloride profile. This particular solution (eqn. 8.3) to Fick's second law is only valid when the assumptions for the boundary conditions correspond reasonably well with the situation in reality.

For two concretes with the same apparent diffusion coefficients, with concrete A having double the surface chloride level compared to concrete B, the chloride level within concrete A would be double that of concrete B at the same depth and at equal times.

The chloride level in the concrete pore solution adjoining the surface, $c_{s,f}$ (moles/cm^3) depends on factors such as the chloride concentration of the solution in contact with the concrete, and evaporation effects in the exposure zone. The evaporation of water would leave salts behind and increase the surface chloride concentration. Regular flushing with water, as found in the tidal zone, would prevent this build up in chloride concentration, but members in the splash zone exposed to the wind and sun could have very high surface chloride

concentrations because of evaporation. The total surface chloride level, C_s (% chloride with respect to cement mass), would depend on additional factors such as cement type and content, concrete porosity and chloride binding.

8.2.2 The effect of chloride binding on chloride diffusivity

As chloride ions enter concrete, some remain in the pore solution, and some are adsorbed onto and chemically combined in the solid matrix. These bound ions can only move by desorption into the liquid with which they are in equilibrium, and therefore effectively reduce the rate of chloride ingress. The capacity of concretes to bind chloride ions differs significantly between different cement types and different cement contents, hence chloride binding is a very important material parameter influencing chloride ingress.

Chloride binding reduces the rate of increase in chloride concentration with time ($\partial c/\partial t$) and hence reduces the apparent diffusion coefficient, D_a (see equation 8.1). Chloride binding does not influence the steady state diffusion coefficient, D_s[1]; however, both D_a and D_s could be affected should the presence of chloride ions alter the pore structure of the concrete. Both D_a and D_s of concrete also change with time as the concrete changes due to additional hydration, etc. Diffusivity determinations from chloride profiles using Fick's Second Law would yield apparent diffusivities, but diffusivity determinations from laboratory steady state diffusion tests or conduction tests would yield values related to the steady state diffusion coefficient[2]. It is therefore important to know to what extent the apparent diffusivity is influenced by binding effects before long term predictions can be made from laboratory tests.

For unidirectional diffusion the principle of mass conservation requires that over any small length (dx) along the diffusion path the change in the ionic flux ($\partial J_{x,m}$) should balance the change in the total quantity (free and bound) of ions present ($\partial c_m/\partial t$) (Sergi et al, 1992),

where c_m ... chloride concentration in medium (free and bound ions) with respect to volume of medium.

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[1] D_s is defined as the flux of chloride ions that would flow through the porous material under a unit concentration gradient in the pore solution.

[2] Most diffusion tests fail to eliminate factors such as diffusion potentials and osmosis, and most conduction tests are empirical.

$$\frac{\partial J_{x,m}}{\partial x} = - \frac{\partial c_m}{\partial t} \qquad (8.5)$$

The change in chloride flux through the medium is therefore dependant on binding phenomena.

At any point in the medium, at any time, the chloride flux through the medium is related to the concentration gradient in the pore liquid by the steady state diffusion coefficient, D_s,

$$J_{x,m} = -D_s \frac{\partial c_l}{\partial x} \qquad (8.6)$$

where c_l ... chloride concentration in pore liquid (free ions) with respect to volume of the pore liquid.

Combining equations 8.5 and 8.6 gives,

$$\frac{\partial c_m}{\partial t} = D_s \frac{\partial^2 c_l}{\partial x^2} \qquad (8.7)$$

Binding phenomena can be characterised by the parameter α which relates c_m to c_l ($c_m/c_l = \alpha$), in which case the equation becomes,

$$\frac{\partial c_m}{\partial t} = \frac{D_s}{\alpha} \frac{\partial^2 c_m}{\partial x^2} \qquad (8.8)$$

or

$$\frac{\partial c_l}{\partial t} = \frac{D_s}{\alpha} \frac{\partial^2 c_l}{\partial x^2} \qquad (8.9)$$

assuming $c_m/c_l = \alpha$ is constant (i.e. linear binding).

By comparison with equation (8.1),

$$D_a = \frac{D_s}{\alpha} \tag{8.10}$$

It can therefore be seen that for an ionic species with linear binding characteristics (α const.), interpolation of both the experimental free and total ionic profiles using Fick's Second Law yields the same value for the apparent diffusivity (Sergi et al, 1992), as can be seen in figure 8.2:

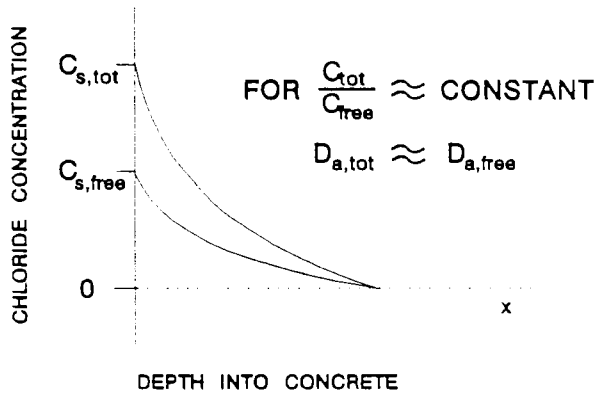

Figure 8.2: Total and free chloride profiles.

8.2.2.1 Non-linear chloride binding

For linear adsorption phenomena, the term α (c_m/c_f) is constant. This is a simplification since chloride binding in concrete is not linear (Tang and Nilsson, 1993) and the bound-to-free ratio varies with concentration.

$$\alpha = \frac{\partial c_m}{\partial c_f} = f(c_f) \tag{8.11}$$

At low chloride concentrations, a greater portion of the ions will be bound, in contrast with higher concentrations when a greater portion will be free (see figure 8.3).

Non-linear chloride binding would result in the following (Nilsson et al, 1994):

1. Free chloride profiles and total chloride profiles would yield different apparent diffusivities (Sergi et al, 1992).
2. The apparent diffusivity will not be constant and will depend on depth and time as it

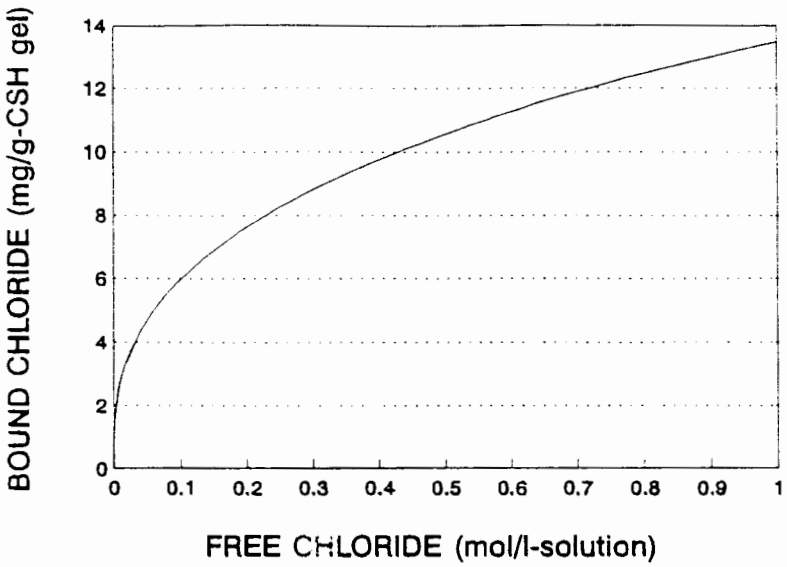

Figure 8.3: Relationship between bound and free chlorides (Tang and Nilsson, 1993).

becomes a function of chloride concentration.

3. The relationship between the apparent diffusivity and the steady state diffusivity will therefore also not be constant.

8.2.3 Chloride diffusion through non-saturated concrete

Ionic diffusion can occur only if water is present in the concrete pores. When the water content decreases, the diffusion process is hindered by the decrease of the number of porous channels which have a continuity of pore solution, and because of the strong rise of the interaction forces between cement paste and ions due to the decrease of the thickness of the adsorbed water layers. When the relative humidity inside the concrete, h, drops below a critical value, h_c = 75 %, the ion diffusivity shows a dramatic drop (Saetta et al, 1993).

8.2.4 The dependence of diffusivity on time

Work by Mangat and Molloy (1994) indicates that the apparent chloride diffusivity of concrete decreases with time. The continuous hydration of concrete, pore blocking mechanisms such as carbonation, and the precipitation of salts could all reduce the diffusivity of concrete. The diffusivity of concrete would also decrease with depth since the outer layer will have relatively less coarse aggregates, more capillary pores, inadequate curing and

would have a more open pore structure due to leaching. This reduction in diffusivity with depth will cause the diffusivity to appear to reduce with time as chloride ions move deeper into the concrete.

For the accurate long-term prediction of chloride diffusion into concrete, the time-dependence of diffusion coefficients needs to be incorporated in the analysis procedure.

The relationship between D_t (apparent diffusivity at time t, see later) and D_{in} (apparent diffusivity initially, t = 1 sec) can be approximated by (Mangat and Molloy, 1994),

$$D_t = D_{in} t^{-m} \tag{8.12}$$

where m is obtained by plotting log D_t against log t, ie. the linear form of the equation,

$$\log D_t = \log D_{in} - m \log t \tag{8.13}$$

The factor m was found experimentally by Mangat and Molloy to depend on the water/cement ratio of the mix,

$$m = 2.5\left(\frac{w}{c}\right) - 0.6 \tag{8.14}$$

These findings were questioned by Mackechnie (1996) since the exposure periods used were short (< 2 years), and would therefore be substantially influenced by the surface chloride concentration which is still increasing at this time. Equation 8.14 would yield values for m above 1 for w/c ratios of more than 0.64 which implies that the direction of chloride diffusion has reversed (see equation 8.22) ! Further, equation 8.14 shows that, for w/c < 0.24, m < 0, which implies D_t increases with time, also physically impossible. Mackechnie calculated m from longer term data obtained from Bamforth (1995) (see table 8.1). The factor m was found to depend on cement composition:

Table 8.1: Reduction factors (m) for different cements (Mackechnie, 1996).

OPC	Fly ash	Slag
m = 0.18	m = 0.67	m = 0.68

The time dependence of the (time-integrated) apparent diffusivity, D_a, can be incorporated in the standard model for chloride diffusion based on Fick's second law by substituting equation 8.12 into equation 8.1,

$$\frac{\partial c_m}{\partial t} = D_{in} t^{-m} \frac{\partial^2 c_m}{\partial x^2} \tag{8.15}$$

Substituting

$$\partial T = (D_{in} t^{-m})\ \partial t \tag{8.16}$$

into equation 8.15 gives,

$$\frac{\partial c_m}{\partial T} = \frac{\partial^2 c_m}{\partial x^2} \tag{8.17}$$

which has the standard solution,

$$C_{x,t} = C_s[1 - erf(\frac{x}{2\sqrt{T}})] \tag{8.18}$$

Integrating ∂T (equ. 8.16) gives,

$$\begin{aligned} T &= \int_0^t D_{in} t^{-m}\ \partial t \\ &= \frac{D_{in}}{1 - m}\ t^{(1 - m)} \end{aligned} \tag{8.19}$$

Substituting this in the standard solution into equation 8.18 yields the final solution,

$$C_{x,t} = C_s[1 - erf(\frac{x}{2\sqrt{\frac{D_{in}}{1 - m}\ t^{(1 - m)}}})] \tag{8.20}$$

It is important to distinguish between the various chloride diffusion coefficients dealt with in this thesis:

D_s ... Steady state chloride diffusion coefficient. It is defined as the flux of chloride ions that would flow through concrete under a unit Cl^- concentration gradient in the pore solution. Chloride binding affects D_s only if the physical pore structure is altered (see 8.2.2).

D_a ... Apparent chloride diffusion coefficient (integrated: t = 0 to t = $t_{current}$). D_a is obtained by applying Fick's second law to a chloride profile (equation 8.3). Chloride binding affects D_a both due to a reduction in $\partial c/\partial t$ and due to possible changes in the physical pore structure. D_a is therefore a function of D_s and the binding paramater α (see equation 8.10).

D_{in} ... Initial (apparent) chloride diffusion coefficient at t = 1 sec. D_{in} can be determined from D_s or D_a if the reduction factor m is known (see equations 8.12 and 8.21).

D_t ... Current (apparent) chloride diffusion coefficient at time t. Differs from D_a, as D_a is an integrated value over the entire period t, while D_t is the actual (instantaneous) diffusion coefficient at time t.

From equations 8.3, 8.12 and 8.20 the relationship between D_a and D_t can be calculated:

From eq. 8.3 and 8.20,

$$D_a = \frac{D_{in}}{1 - m} t^{-m} \qquad (8.21)$$

Substituting eq. 8.12 into this equation gives,

$$D_a = \frac{D_t}{1 - m} \qquad (8.22)$$

8.2.5 The dependence of diffusivity on temperature

Diffusion through concrete is substantially influenced by temperature, as is diffusion in free

water. With diffusion through concrete, additional temperature-dependant factors are included. Page et al (1981) and Goto and Roy (1981) showed that activation energies associated with chloride diffusion were much higher in cement compared with chloride diffusion in free water. Atkinson and Nickerson (1984) postulated that this change was as a result of changes in the pore structure with temperature, and not just because of the diffusion mechanism.

Cement hydration is also affected by temperature, and the effect of temperature differs for different cement types. Dhir et al (1993) showed that the resistance of fly ash concretes to chloride ingress was improved dramatically at higher temperatures compared with similar OPC mixes.

8.2.6 The effect of other ions on diffusion

The cations associated with the chloride ions entering concrete as well as the ions present in the concrete can influence chloride ingress.

The difference in mobility between the partner ions would create a diffusion potential which would affect the rate of diffusion of both species. The diffusion potential could also lead to the migration of other ions present in the concrete. Yu et al (1993) showed that the diffusion of both sodium and chloride ions in concrete can be modelled by Fick's second law, but that the movement of the hydroxyl ions was so as to maintain the charge balance in the system.

The cations associated with the chloride ions would also influence the binding characteristics of the concrete, and hence influence the apparent diffusion coefficient (Arya and Newman, 1990).

8.2.7 Summary

Chloride ingress into concrete can be modelled by Fick's second law for non-steady state diffusion provided diffusion is the main mechanism of chloride ingress. A linear solution to the equation can be obtained assuming the surface chloride level reaches a constant value in a short period of time.

Analysing total chloride profiles or free chloride profiles using this equation would yield the same apparent diffusion coefficient, D_a (assuming linear binding characteristics). The relationship between the apparent diffusion coefficient, D_a, and the steady state diffusion coefficient, D_s, would then depend on the binding capacity of the concrete.

The chloride diffusivity of concrete changes significantly with time. This time dependence of D needs to be incorporated in chloride ingress models. The diffusivity of concrete is substantially influenced by temperature, the saturation level of the concrete, and the cations associated with the chloride ions. Hence, it is not a fundamental material property as it is influenced by the environment and changes with time.

8.3 CORRELATION STUDY: SERIES 2 TESTS

The objectives of this section is to demonstrate the feasibility of using the chloride conduction test in a long-term chloride ingress model, and to provide a basis for future correlation studies. The experimental details relating to this study is included in chapter 4, and the bulk results in Appendix 2 Part B.

8.3.1 Calculation of D_a and C_s

A QPRO spreadsheet program was written to solve the apparent chloride diffusion coefficient, D_a, and the surface chloride content, C_s (extrapolated), given the four chloride contents at various depths.

The solution to the error function (erf) is shown in table 8.2, column 2. Two least squares curves were fitted to the error function; one between $0 < x < 0.4$, and one between $0.4 < x < 2$. This was done in order to obtain an approximate solution to the error function which could be coded into a spreadsheet programme. The coefficients of the polynomials of the least squares curves are shown in table 8.3. The least squares curves are plotted in figure 8.4. The actual solutions, the least squares solutions and the respective error percentages are shown in table 8.2. The error percentages are all low which indicates a good fit between the least squares curves and the error function.

Table 8.2: Solution to the error function; erf(x).

x	erf(x)	Fitted curve	Error
0	0.0000	0.0000	0.00%
0.1	0.1125	0.1145	1.80%
0.2	0.2227	0.2241	0.61%
0.3	0.3286	0.3287	0.03%
0.4	0.4284	0.4284	0.00%
0.5	0.5205	0.5243	0.73%
0.6	0.6039	0.6084	0.75%
0.7	0.6778	0.6815	0.54%
0.8	0.7421	0.7444	0.30%
0.9	0.7969	0.7978	0.12%
1	0.8427	0.8427	0.00%
1.1	0.8802	0.8798	0.05%
1.2	0.9103	0.9099	0.05%
1.3	0.9340	0.9337	0.03%
1.4	0.9523	0.9523	0.00%
1.5	0.9661	0.9662	0.01%
1.6	0.9763	0.9763	0.00%
1.7	0.9838	0.9835	0.03%
1.8	0.9891	0.9886	0.05%
1.9	0.9928	0.9922	0.06%
2	0.9953	0.9953	0.00%

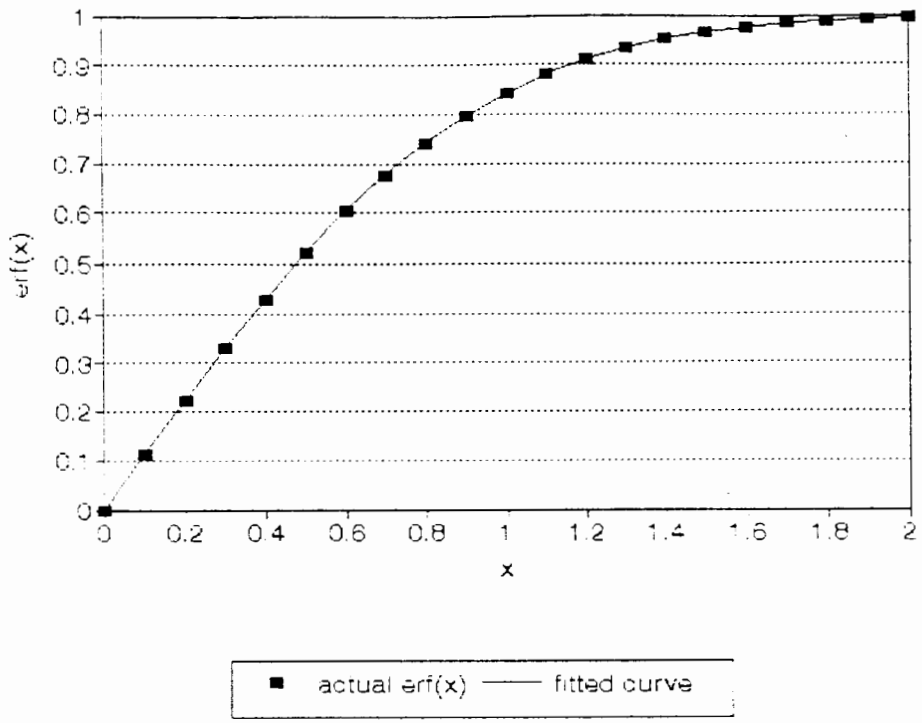

Figure 8.4: Least squares curve fitted to the error function.

Table 8.3: Coefficients of the polynomials of the least squares curves fitted to the error function.

Polynomial coefficients			
for x > 0.4		for x < 0.4	
-0.0895	1	-3.5809×10^{-6}	1
1.5902	x	1.1695	x
-0.7920	x^2	-0.2457	x^2
0.1341	x^3		

The program starts by estimating C_s by fitting a least squares curve to four measured points (see figure 8.5 and table 8.4).

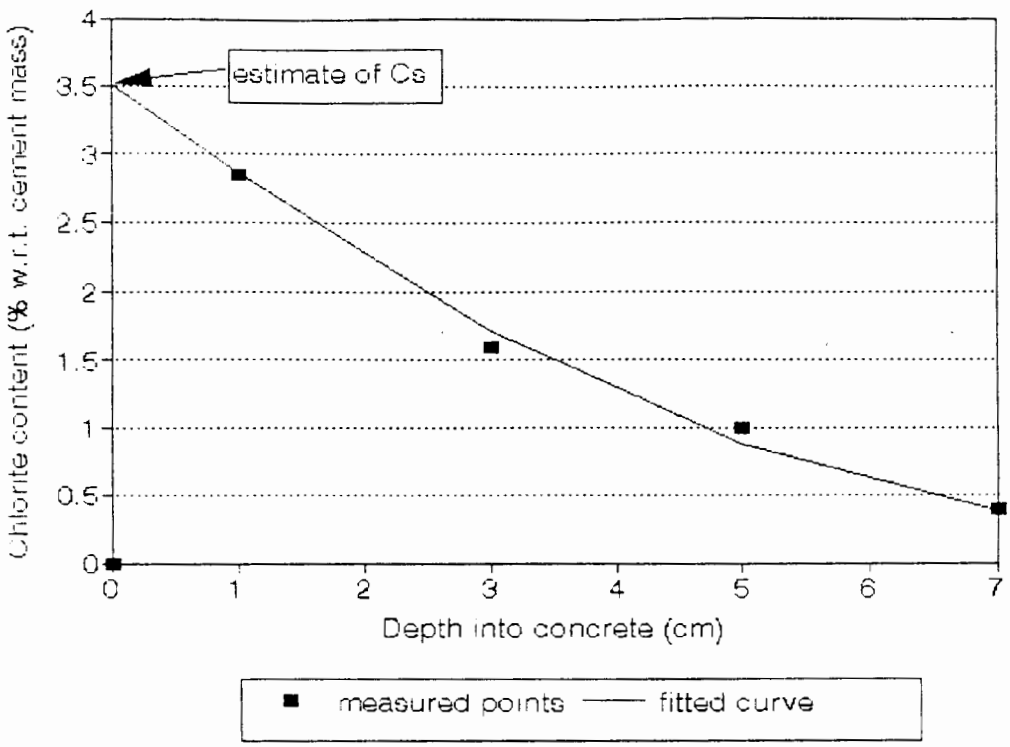

Figure 8.5: Least squares curve fitted to four measured points.

Table 8.4: Least squares fit to estimate C_s.

x (cm)	Measured [Cl] (w.r.t. cement mass)	Least squares estimate ([Cl] w.r.t. cement mass)
0	-	3.50
1.00	2.80	2.80
3.00	1.60	1.70
5.00	1.00	0.90
7.00	0.40	0.40

C_s estimate = 3.50 % w.r.t. cement mass.

An iteration procedure is then used to determine the best estimate D_a value for the first C_s estimated (see table 8.5). The squared differences between the four measured points are calculated and minimised to obtain the best estimate D (row 4).

Table 8.5: Optimum D_a for given C_s.

D_a (cm^2/s)	Squared Differences
1.31e-07	0.0039031
1.32e-07	0.0035927
1.33e-07	**0.0034920**
1.34e-07	0.0036650

C_s is then increased or decreased based on a visual assessment of the fitted curve. Another iteration procedure is performed to determine the optimum D value for the second C_s estimate. The squared differences between the fitted curve and the measured points are again calculated and compared with that of the first C_s curve.

This procedure is continued until C_s and D are optimised, based on the lowest overall squared differences, to three significant figures.

8.3.2 Correlation between apparent diffusivity and chloride conductivity

The philosophy behind examining the correlation between diffusivity and conductivity is that conductivity (σ) is linearly related to steady state diffusivity (D_s), and apparent diffusivity (D_a) is a function of steady state diffusivity and the chloride binding capactity (α). The exclusion of a parameter for chloride binding might result in different correlations for different cement types (as binding is a function of cement type).

The one year apparent diffusion values, $D_{a,\ 1y}$, are plotted against the 1, 7 and 28 day wet cured chloride conduction values in figures 8.6, 8.7 and 8.8 respectively. Figure 8.9 is a re-plot of figure 8.7, but distinguishing between the Portland cements and the blends. Regression analyses were performed to obtain the best fit straight lines to each data set. Correlation coefficients were calculated for each fit. The best fit was obtained with the 7 day wet cured chloride conduction values ($r = 0.92$) (see figure 8.7). The correlations were poorer with the 1 and 28 day wet cured chloride conduction values (1d: $r = 0.83$, 28d: $r =$

0.88) (see figures 8.6 and 8.8). The correlation equation for the regression line shown in figure 8.7 was calculated to be:

$$\log_{10} D_{a,1y} = 0.64\sigma_{7d} - 8.1 \qquad (8.23)$$

(for D_a in cm^2/s, σ in mS/cm)

The factors that affect the correlation coefficient are listed below:

1) Variability of D_a calculated from chloride profiles (section 8.3.4).
2) Variability of σ (see chapter 7).
3) The actual correlation between σ and D_a:
   - 3.1) D_a includes some mechanisms which are not included in σ (ie. chloride binding; see section 8.2).
   - 3.2) The assumptions used in determining D_a are not entirely accurate (ie. surface chloride levels are not constant; see sections 8.2.1.1 and 8.4.3).

At this stage the variability of D_a (section 8.3.4) is still unknown, so it is difficult to say what the variability of the actual correlation between D_a and σ is. However, it will be possible in future to determine the variability of D_a by correlating 1 year D_a values with 2 year D_a values.

Note that the blocks were wet cured for 3 days initially. The fact that the best correlation was achieved with the 7 day chloride conductivity values and not the 28 day values indicates the possibility that delayed curing (which was likely to occur in the tidal zone) has had little effect. Initial wet curing of 28 days instead of 7 days would have favoured the blended mixes (lower conductivity) which are more sensitive to curing at this stage. The results therefore indicate the importance of initial curing especially for the blended cement mixes. Note however that at this early stage (1 year), the chloride profile has generally not entered very deeply into the concrete, and is influenced by the near-surface layer of the concrete which is most affected by inadequate curing. As the chlorides enter deeper into better cured concrete the best correlation might well be found with the 28 day wet cured chloride conductivity values.

The correlation between $D_{a,1y}$ and the 7 day wet cured **2 week** conductivity values gave a similar correlation coefficient ($r = 0.92$) compared with that of the 7 day chloride

conductivity values.

At this stage (after 1 year) there was no strong evidence to suggest that the correlation differed for the different cement types (see figure 8.9). It is however expected that the apparent diffusion coefficients will decrease with time and at different rates (Mangat and Molloy, 1994) as chloride ions enter deeper into the (better quality) concrete, and as the concrete continues to hydrate. The concretes which are sensitive to curing (blended mixes) should have the greatest gradient in quality with depth and also the greatest change in properties over the long term, leading to a greater reduction in diffusion coefficients with time. This implies that at later ages, the correlation (between apparent diffusion coefficients and chloride conductivity values) might well differ for different cement types. It is envisaged that the reduction in diffusivity with time could be correlated to the reductions measured in the 2 week chloride conduction test.

Chloride profiles after 1 year for a range of chloride conductivity values are plotted in figure 8.10 based on equation 8.3 and the correlation equation 8.23. The dimensionless ratio C_x/C_s is plotted on the Y-axis. To obtain the chloride profile for a specific mix, the profile in figure 8.10 must be multiplied by an appropriate surface chloride level (see section 8.4). Figure 8.11 shows the confidence intervals of the chloride profiles corresponding to the 1.0 and 2.0 mS/cm chloride conductivity values. It can be seen from figure 8.11 that the intervals are fairly narrow and do not overlap for the two chosen values. A 20 % lower chloride conductivity value would generally be required for the upper 95 % confidence interval.

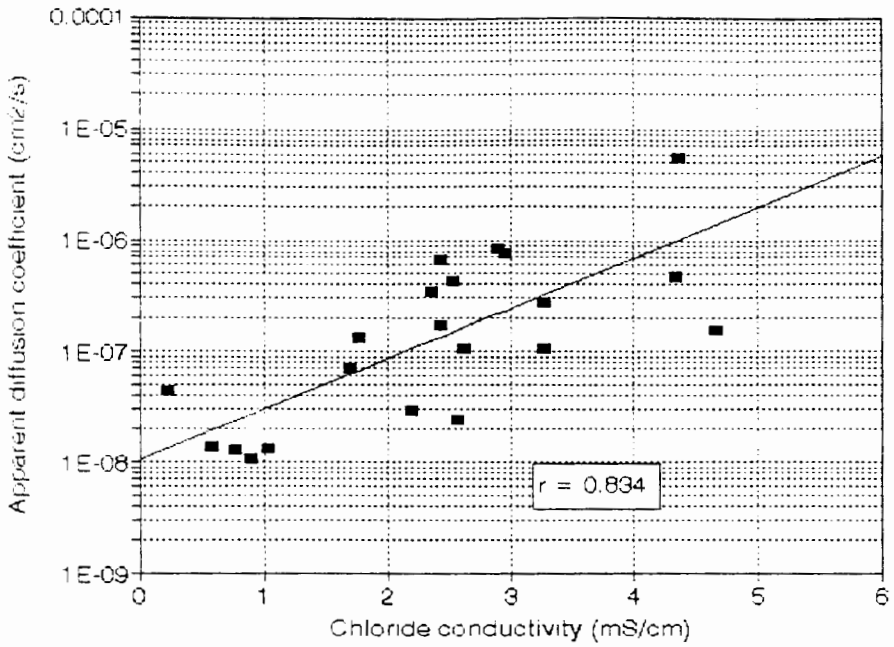

Figure 8.6: Correlation between one year D_a values and 1 day wet cured chloride conductivity values.

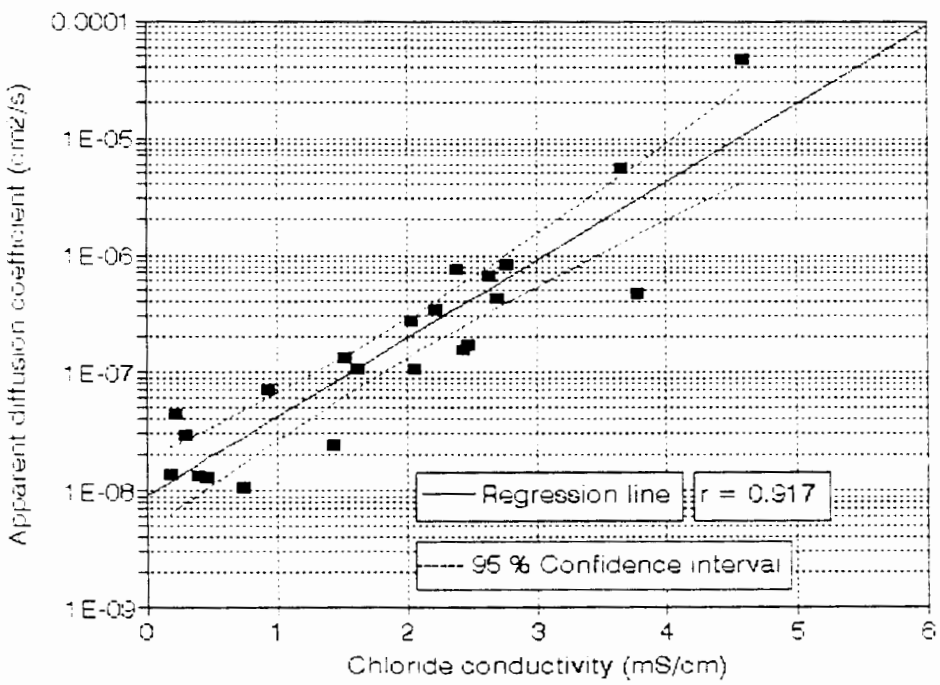

Figure 8.7: Correlation between one year D_a values and 7 day wet cured chloride conductivity values.

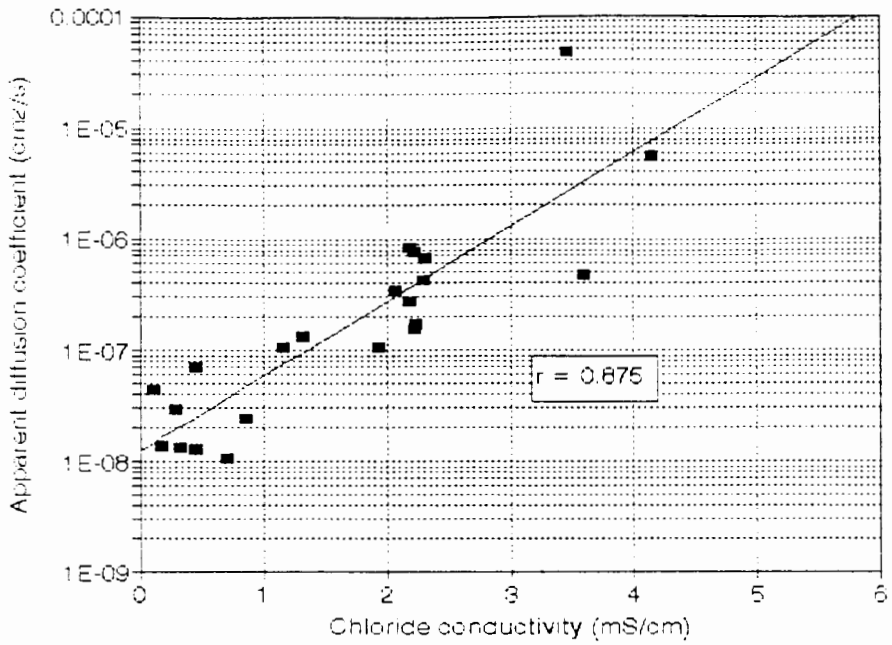

Figure 8.8: Correlation between one year D_a values and 28 day wet cured chloride conductivity values.

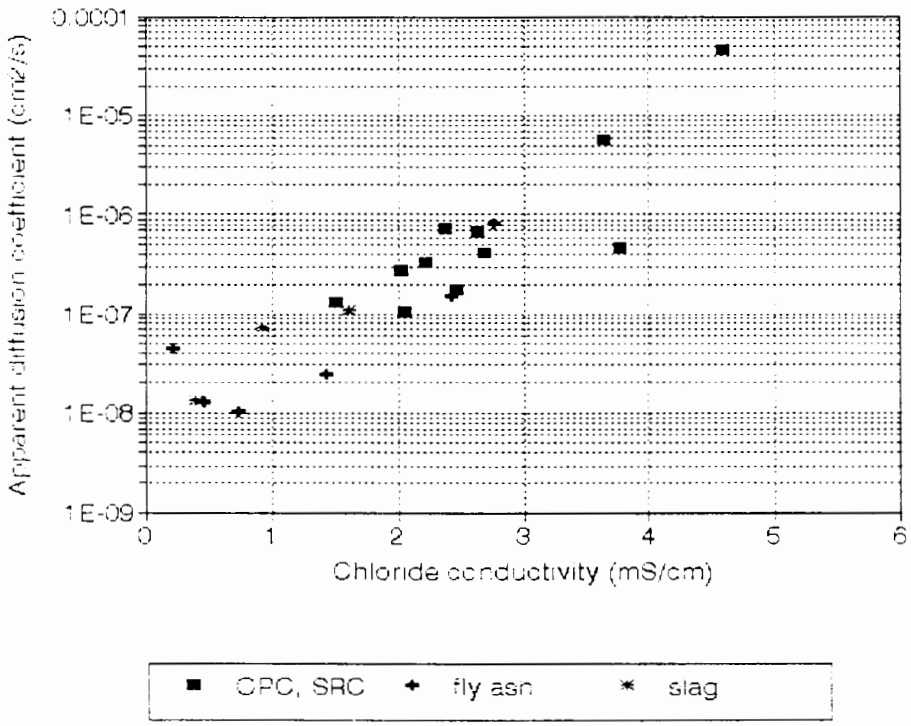

Figure 8.9: Re-plot of figure 8.7, distinguishing between cement types.

From figure 8.11 it can be shown that for a Portland cement concrete with a chloride conductivity of 2.0 mS/cm (w/c 0.5) and a surface chloride level of 1.8 %, the critical chloride level (0.4 %) would be exceeded at a depth of between 36 and 54 mm after only 1 year, with a probability of 95 %. (The critical chloride level is the threshold level where corrosion becomes likely. The value of 0.4 % is generally accepted as a workable threshold level).

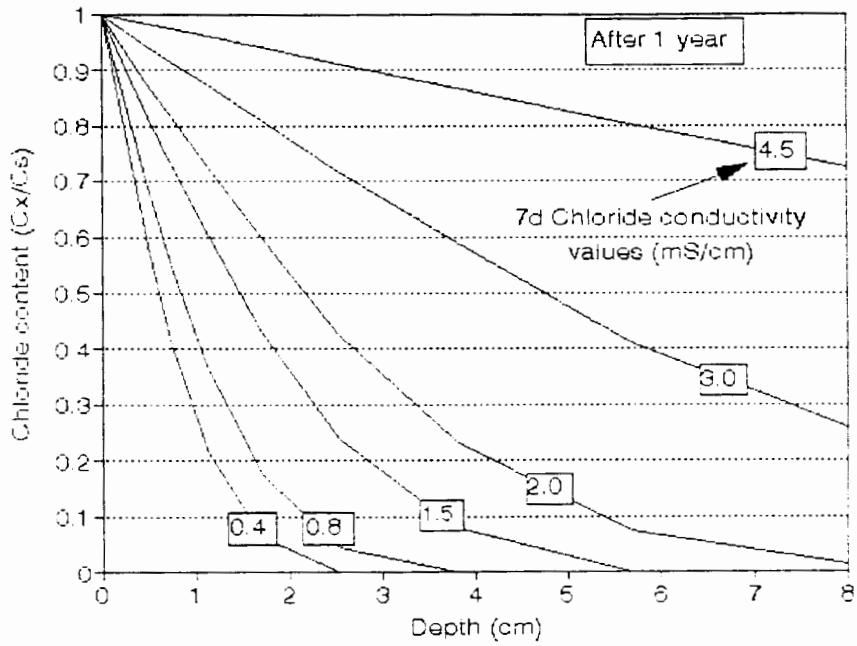

Figure 8.10: Chloride profiles after 1 year for a range of chloride conductivity (mS/cm) values.

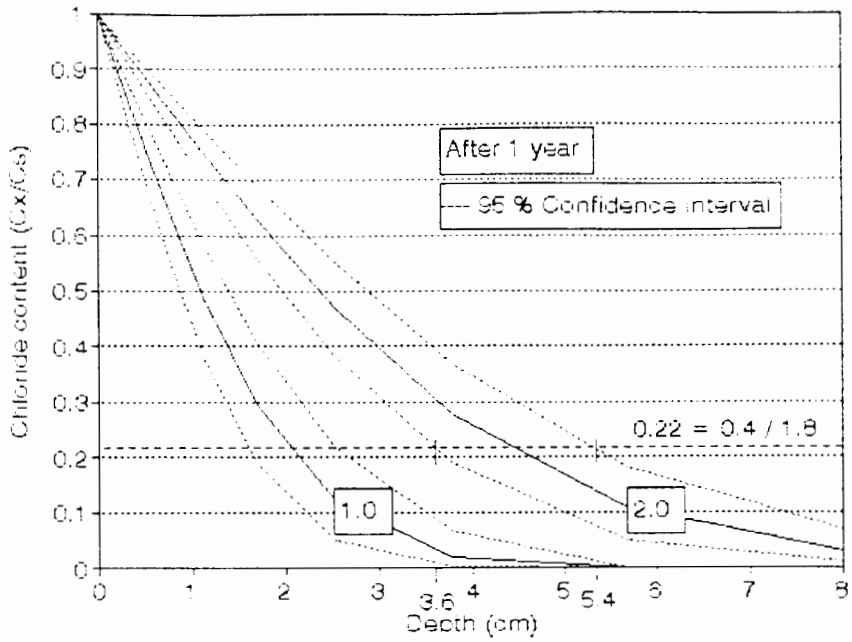

Figure 8.11: Confidence intervals for 1.0 and 2.0 mS/cm chloride profiles (1 year).

8.3.3 Correlation between diffusivity and permeability and sorptivity

The one year apparent diffusion values, $D_{a,1y}$, are plotted against the 7 day wet cured oxygen permeability index values in figure 8.12 and against the 7 day wet cured water sorptivity values in figure 8.13. Regression analyses were performed to obtain the best fit straight line to each data set. Correlation coefficients were calculated for each fit. The correlation coefficients were poorer than those for chloride conductivity ($r = 0.70$ for permeability and $r = 0.75$ for sorptivity). Chloride conductivity appears to be better suited to predict chloride levels in concrete. However, sorptivity and permeability might be better suited to predict other processes such as carbonation, corrosion or chloride ingress due to ponding where the transport mechanisms include gas or water permeation.

The data points of the blended mixes in figure 8.12 were generally below those of the Portland cement mixes which indicates lower apparent diffusion coefficients for similar oxygen permeability indexes. This could be ascribed to the fact that chloride ingress involves different transport mechanisms (diffusion and chloride binding) than gas permeability and is therefore dependant on different properties of the material.

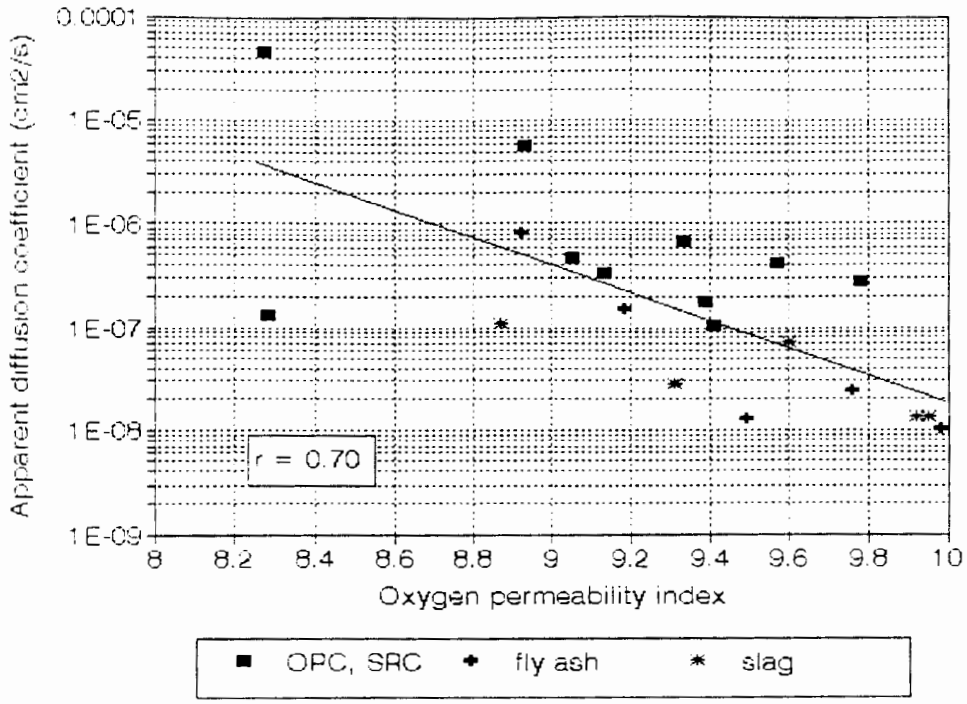

Figure 8.12: Correlation between 1 year D_a and the 7 day wet cured oxygen permeability index values.

There was no strong evidence to suggest that the sorptivity correlation differed for the different cement types (see figure 8.13).

8.3.4 Variability of D_a calculated from chloride profiles

The variability of D_a was ascribed mainly to the nature of chloride profile determinations. There are a number of factors that contribute to this variability:

1) Depth of drilling: It is difficult to drill precisely to the set depth increments. The resulting errors increase as the depth increments are reduced.
2) Composition of drillings: Two holes of 20 mm diameter were drilled, while the nominal coarse aggregate size was 19 mm. The cement content of each drilling is therefore variable. (In retrospect, it might have been better to drill 3 holes.)
3) The chloride content of each drilling is plotted in the centre of that depth increment (see figure 8.14). If the plotted profile has a high degree of curvature, the error of this approximation becomes notable.
4) If the chosen depth increments do not match the profile sufficiently, the above factors become increasingly significant (see figure 8.15). With very permeable concretes it

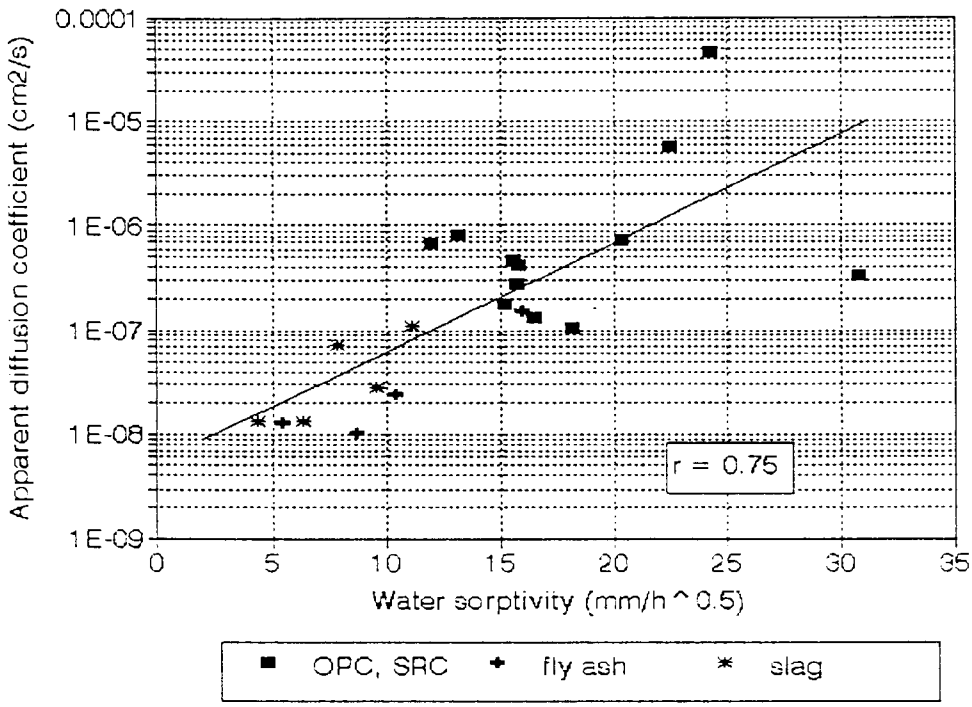

Figure 8.13: Correlation between one year D_a and the 7 day wet cured water sorptivity values.

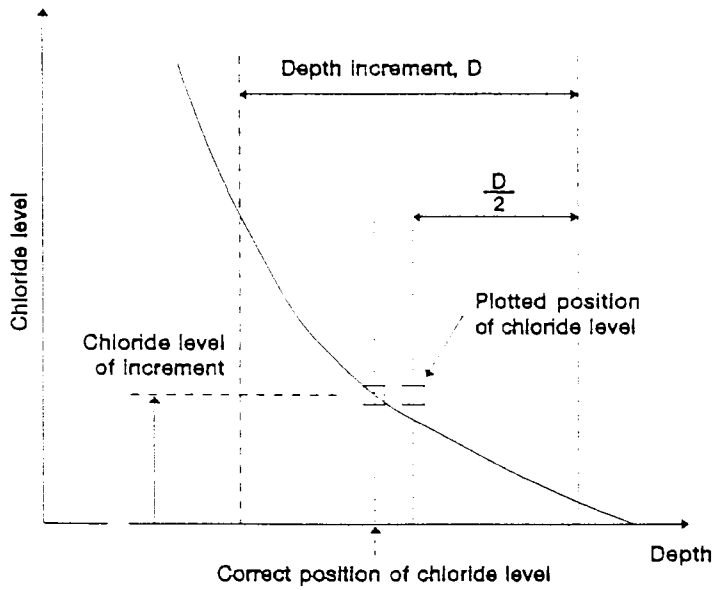

Figure 8.14: Effect of position of chloride level within depth increment.

is possible to increase the depth increments; however with the more impermeable concretes there is a limit to which the depth increments can be reduced. Fortunately this problem will reduce with time as the chloride ions enter deeper into these

concretes.

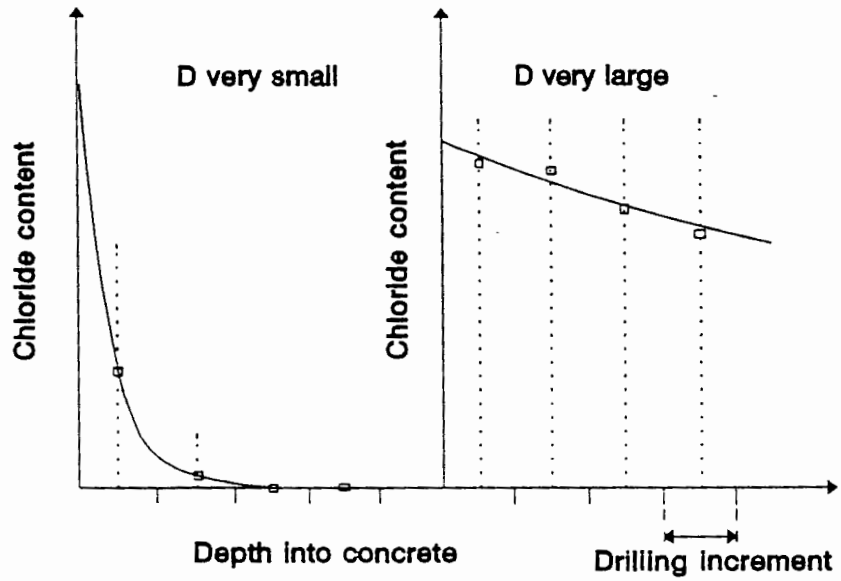

Figure 8.15: Chloride profile determinations with unsuitable depth increments.

It is likely to be better to use a profile grinding procedure instead of a drilling procedure for chloride profile determinations. A larger surface area could then be sampled. Such equipment is commercially available (German Instruments).

8.3.5 Conclusions

A good correlation (r = 0.92) was found between the 7 day wet-cured chloride conductivity values, and the one-year apparent chloride diffusion coefficients of the in-situ concrete blocks (3 days wet cured initially). The correlations with both the 1 and 28 day conductivity values were poorer (r = 0.83 and 0.88 respectively). The good correlation shows promise for the development of a chloride ingress model based on the chloride conductivity test.

These correlations were substantially better than those between the oxygen permeability and water sorptivity results and the apparent chloride diffusion coefficients (r = 0.70 and 0.75 respectively). This indicates the mechanism of chloride ingress was predominantly diffusion and not permeation or absorption.

At this early stage (after 1 year) there was no strong evidence to suggest that the correlation

differed for the different cement types. It is however expected that the apparent diffusion coefficients of the different cements will decrease with time at different rates (Mangat and Molloy, 1994). This will lead to differences in correlations for different cement types. At this early stage, the variability of the apparent diffusivity determinations is high, hence it is difficult to observe these trends.

It is believed that the correlation coefficient is influenced substantially by the variability of the apparent diffusivity determinations. This issue was investigated in the correlation study performed in the series 1 tests.

The use of a coring procedure instead of a drilling procedure for chloride profile determinations was proposed to reduce variability.

8.4 IN-SITU CHLORIDE INGRESS PARAMETERS (SERIES 1 TESTS)

8.4.1 Introduction

Chloride ingress into concrete is generally modelled using a solution equation derived from Fick's Second Law for non-steady state diffusion. A chloride profile can be characterised by a surface chloride content (C_s) and an apparent chloride diffusion coefficient (D_a). These parameters are inter-related in terms of variability as a higher estimated C_s for a specific chloride profile will result in a lower estimate for D_a.

The "apparent" chloride diffusion coefficient is so named since it is influenced by both the physical resistance of the concrete to chloride ingress (steady state diffusivity (D_s)) and the chemical resistance of concrete to chloride ingress (chloride binding capacity (α)) (Atkinson and Nickerson, 1984). Depending on the binding capacity, D_s can be 3 times higher than D_a (Sergi et al, 1992). Note that D_s can be affected by chemical effects should the physical pore structure be altered by the presence of chloride ions.

In this work, D_a has been correlated with results from laboratory steady state chloride diffusion tests and rapid chloride tests. Laboratory steady state diffusion tests, as well as

steady state **and** non-steady state rapid chloride tests generally determine or estimate D_s (Tang and Nilsson, 1995). Predicting chloride ingress in-situ from laboratory chloride tests would then involve converting D_s to D_a using the correlation equation, and then substituting a suitable C_s value into the solution equation. Note that D_s does not include the effect that chloride binding has on non-steady state diffusion (Sergi et al, 1992). Correlations would therefore differ for cements which differ in chloride binding capacity.

Bamforth (1994) and Mackechnie (1996) have shown that in-situ surface chloride levels fluctuate in the early stages of chloride ingress ($<$ 2 years). This is most likely due to the inherent variability in determining C_s, which is an extrapolated value (extrapolation accuracy is poor at early ages due to the steepness of the chloride profile). Using the prediction procedure described earlier, the inherent variability of C_s would be included twice - in the estimation of D_a for the correlation relationship, and in the solution equation for long-term predictions. An approach that involves a chloride ingress parameter which combines D_a and C_s might therefore be more suitable for chloride ingress models.

8.4.2 Scope and objective

The concrete mixtures reported here included blends of two types of silica fume (densified and undensified) with normal portland cement. A non-blended portland cement was used as the control. Three target strengths, 25, 50 and 75 MPa, and two replacement levels of 5 % and 10 % were used. Cubes were cast, subjected to moist-curing and laboratory air-curing regimes, and tested for compressive strength and resistance to chloride transport. Other cube specimens were transported to the exposure site, placed in submerged, tidal and spray marine zones and tested after 2 years for chloride ingress.

The objective of this section is determine which in-situ chloride ingress parameter is the most suitable for chloride ingress models.

8.4.3 Experimental programme

The experimental details are included in chapter 4, while the rapid chloride testing is dealt with in chapter 5 (test method) and Appendix 1 (test results).

The first set of exposed cubes was transported to the laboratory after 2 years, and the chloride profiles were determined. This was done by drilling three 20 mm diameter holes in each cube. The depth increments depended on the concrete grade:

25 MPa - 4 x 20 mm depth increments

50 MPa - 4 x 15 mm depth increments

75 MPa - 4 x 10 mm depth increments

Ideally the depth increments should be chosen so that the critical chloride level lies in the third depth increment (20 MPa: 40-60mm; 50 MPa: 30-45mm; 75 MPa: 20-30mm). This was approximately achieved (see table 7) with the 25 and 50 MPa concretes (56-70mm and 29-51mm respectively), but not with the 75 MPa concretes (11-16mm). This meant that the data for the 75 MPa concretes probably had a higher variability.

The total chloride contents were determined in accordance with BS1881, using a Mettler auto-titrator. The percentage total chloride content with respect to cement mass was calculated.

Apparent chloride diffusion coefficients, D_a, and surface chloride levels, C_s, were calculated using a solution (equation 8.24) to Fick's Second law (equation 8.25).

$$\frac{\partial c_m}{\partial t} = D_a \frac{\partial^2 c_m}{\partial x^2} \qquad \textbf{(8.24)}$$

where c_m ... chloride concentration in the medium

t ... time

x ... depth into the medium

D_a ... apparent diffusion coefficient

$$C_{x,t} = C_s[1 - erf(\frac{x}{2\sqrt{D_a t}})] \qquad \textbf{(8.25)}$$

where erf ... error function

$C_{x,t}$ ... chloride concentration at depth x at time t

C_s ... surface chloride concentration

An iteration procedure was used to determine the best estimate D_a and C_s values, based on a least squares criteria. From D_a and C_s, the depth of the critical chloride level (taken as 0.4

%, i.e. $x_{0.4}$) was calculated (using equation 8.25).

8.4.4 Test results

The compressive cube strengths and the rapid chloride test results are displayed in table 8.6, the apparent chloride diffusion coefficients are displayed in table 8.7, the surface chloride levels in table 8.8, and the depths of the critical chloride levels in table 8.9. The apparent diffusion coefficients after 2 years are plotted against the mean of the 7 and 28 day chloride index values in figure 8.16. The depths of the critical chloride level after 2 years are plotted against the (mean 7d-28d) chloride index values in figure 8.17.

8.4.5 Discussion of results

The results of specimens from the submerged, tidal and spray marine exposure zones did not show any significant trend as a function of exposure zone (see Appendix, series 1 tests). The mean of the three results was therefore calculated and used in the correlations.

Table 8.6: Cube strengths and rapid chloride index values

Binder Type	Mix No.	28 day Target Strength (MPa)	28 day Cube Strength (MPa)	Chloride index (mA)		
				Wet curing period		Mean 7, 28d
				7 day	28 day	
PC	B1 B2 B3	25 50 75	21.2 47.8 69.8	145 49 20.6	116 38 16.5	131 44 18.6
PC – 5% UCSF	B4 B5 B6	25 50 75	22.4 47.6 75.1	126 23.3 8.6	81 15.5 8.9	104 19.4 8.8
PC – 10% UCSF	B7 B8	25 50	19.8 43.2	137 20.4	66 10.9	102 15.7
PC – 5% DCSF	B13 B14 B15	25 50 75	20.4 39.7 60.1	117 34.8 14.0	69 24.1 12.8	93 29.5 13.4
PC – 10% DCSF	B16 B17	25 50	23.1 44.6	96 20.0	52 11.5	74 15.8

Note: Although the experimental programme contained 21 mixes (B1 - B21), only the mixes listed above were selected for the laboratory chloride tests due to time constraints. A full set of mixes was placed at the exposure site.

Table 8.7 : Apparent diffusion coefficients D_a after 2 years

Mix no.	Apparent chloride diffusion coefficient (cm^2/s)			
	Exposure zone			Mean
	Submerged	Tidal	Spray	
B1	1.32e-07	1.91e-07	1.38e-07	1.51e-07
B2	5.20e-08	1.74e-08	4.83e-08	3.52e-08
B3	8.72e-09	3.00e-08	1.47e-08	1.57e-08
B4	1.29e-07	1.41e-07		1.35e-07
B5	2.78e-08	4.31e-08	3.06e-08	3.32e-08
B6	1.12e-08		1.33e-08	1.22e-08
B7	8.32e-08	1.10e-07		9.55e-08
B8	4.32e-08	3.72e-08	2.72e-08	3.52e-08
B13		7.94e-08		7.94e-08
B14	3.65e-08	5.64e-08		4.54e-08
B15	5.87e-09	2.25e-08	1.12e-08	1.14e-08
B16		8.51e-08		8.51e-08
B17	2.66e-08	4.84e-08		3.59e-08

Table 8.8 : Surface Chloride Levels C_s after 2 Years.

Mix no.	Surface chloride level C_s (% w.r.t. cement mass)		
	Exposure zone		
	Submerged	Tidal	Spray
B1	2.52	2.09	3.51
B2	1.97	1.33	2.05
B3	2.70	0.84	1.61
B4	3.69	2.56	
B5	3.20	2.06	2.72
B6	1.88		1.15
B7	4.6	3.44	
B8	1.98	2.87	2.95
B13		4.36	
B14	1.95	1.33	
B15	1.84	1.79	1.88
B16		4.24	
B17	4.52	1.83	

Note: The blank spaces are due to cubes which cracked during the drilling procedure (25 MPa mixes - B4, B7, B13 and B16), or cubes which went missing on site (B6, B14 and B17).

Table 8.9 : Depths of the Critical Chloride Level after 2 Years

Mix no.	Depth of the critical chloride level (cm)			
	Exposure zone			Mean
	Submerged	Tidal	Spray	
B1	6.03	6.72	6.93	6.56
B2	3.41	5.05	3.35	3.94
B3	1.55	1.44	1.64	1.54
B4	6.80	6.29		6.55
B5	3.02	3.17	3.35	3.18
B6	1.59		1.26	1.43
B7	5.80	6.14		5.97
B8	3.12	3.36	2.90	3.13
B13		5.60		5.60
B14	2.85	3.43		3.14
B15	1.11	2.14	1.55	1.60
B16		5.77		5.77
B17	3.28	3.18		3.23

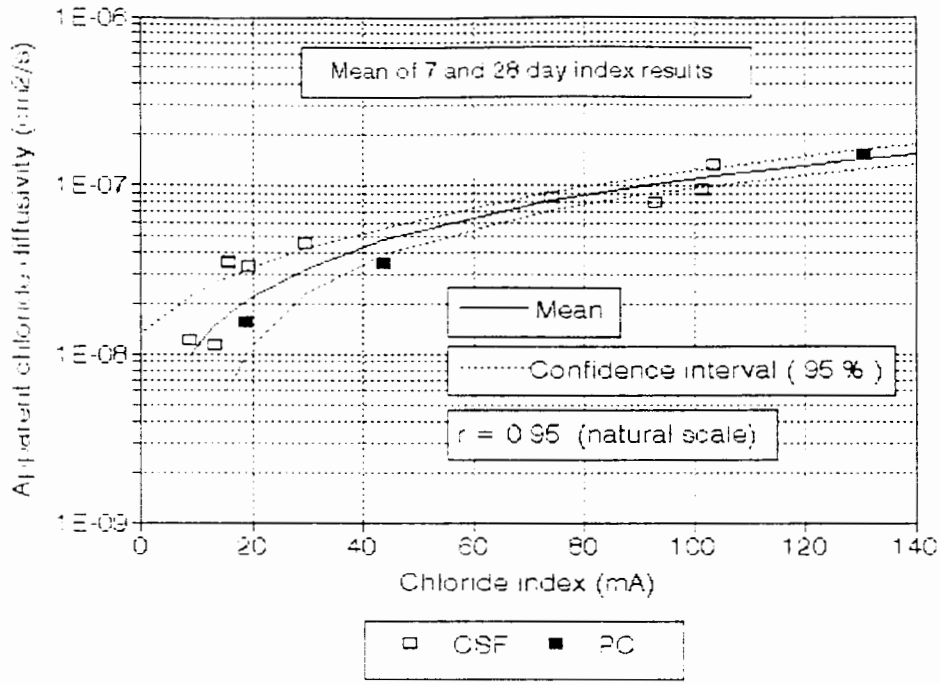

Figure 8.16 - Apparent chloride diffusion coefficients versus the chloride index values

The correlation coefficient (r) between D_a and the chloride indexes (natural scale) was 0.91 for the 7 day values, 0.95 for 28 day values and 0.95 for the mean of the 7 and 28 day wet cured values (see figure 8.16). The fact that the better correlation was obtained with the 28 day wet cured chloride index values indicates that additional curing occurred on-site (the exposure cubes were wet cured for 3 days).

It can be seen in figure 8.16 that the portland cement mixes generally had lower D_a values for similar chloride index values compared with the CSF mixes. This can be ascribed to the lower chloride binding capacity of silica fume mixes (Arya et al. 1990). This trend was more pronounced and more consistent in figure 8.17 where the depth of the critical chloride level was plotted against the (mean 7-28d) chloride index values. The following trends were observed:

1. For similar chloride index levels, $x_{0.4}$ increased with an increase in CSF content.
2. The magnitude of this trend increased with concrete strength (lower left portion of figure 8.17).

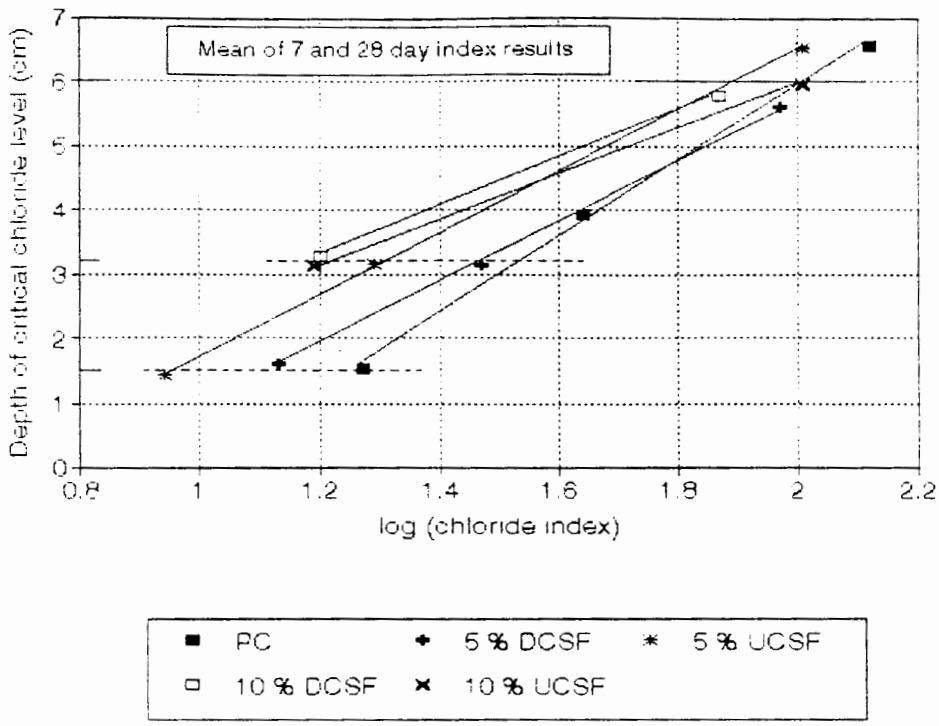

Figure 8.17 - Depth of the critical chloride level (C_x = 0.4 % with respect to cement mass) versus log of the chloride indexes.

CSF mixtures therefore require lower chloride index values to produce depths of chloride penetration similar to those of pure portland cement mixtures. Regression analyses were performed to determine the sensitivity of CSF chloride index values to CSF content.

Since the chloride penetration depths were similar for the CSF mixes of common target strengths (see figure 8.17), the ratio of chloride index values to pure portland cement chloride indexes for specific $x_{0.4}$ values were plotted against CSF content in figure 8.18. The $x_{0.4}$ values chosen were 60 mm for the 25 MPa mixes (see figure 8.18a), 32 mm for the 50 MPa mixes (see figure 8.18b) and 15 mm for the 75 MPa mixes (see figure 8.18c).

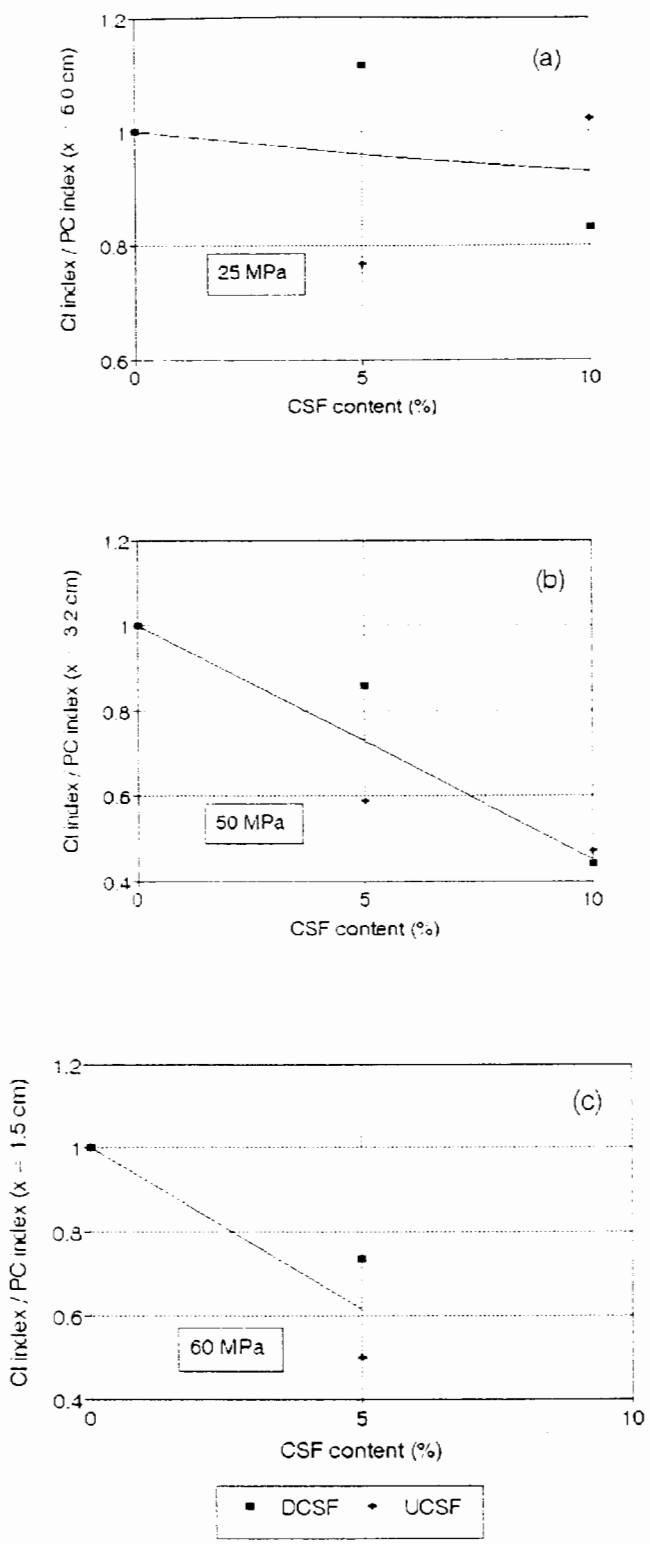

Figure 8.18: Ratios of chloride index values to pure portland cement chloride indexes versus CSF content for critical depths of 60 mm (25 MPa), 32 mm (50 MPa) and 15 mm (75 MPa mixes)

Regression analyses were performed to determine a linear relationship between CSF content and the reduction in chloride index required for each target strength. All chloride index values were then adjusted to that of an equivalent (0 % CSF) portland cement mix. Figure 8.19 shows $x_{0.4}$ plotted against the adjusted chloride indexes. The correlation coefficient between $x_{0.4}$ and the adjusted chloride index values was calculated to be 0.983. This is a substantial improvement compared with the correlation between D_a and the chloride indexes.

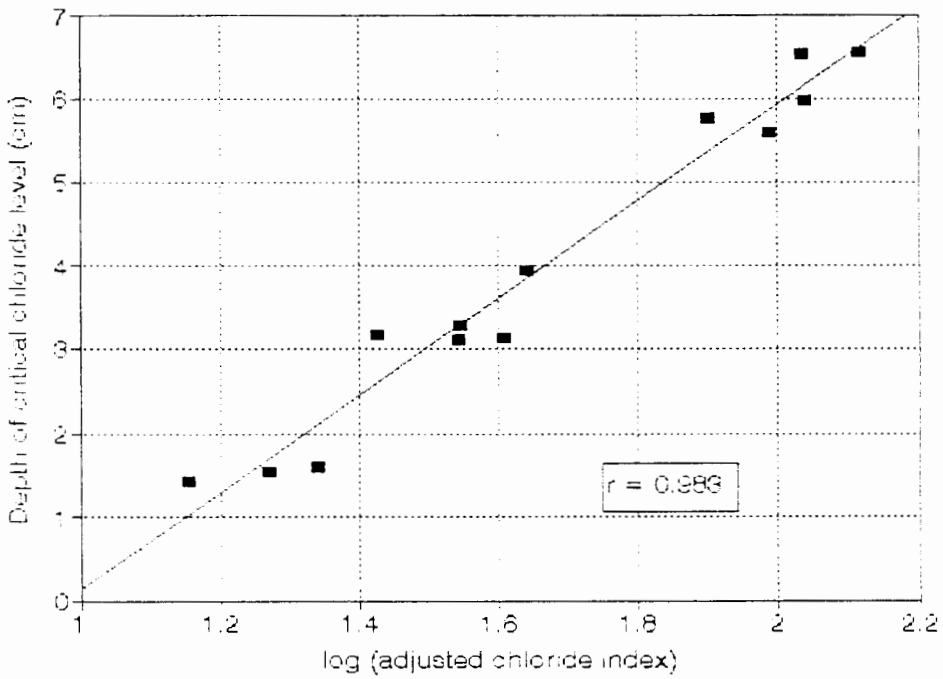

Figure 8.19 - Depth of the critical chloride level versus log of the adjusted chloride index values

Ideally, adjustments to rapid chloride test results should be based on a measurable property incorporating chemical effects, and not just on cement type[3]. Rapid chloride tests determine mainly the physical resistance of concrete to chloride ingress, while on-site, both the physical and chemical (binding effects) properties influence the resistance of concrete to chloride

[3] Some might argue that ideally one should measure a parameter which includes both the physical and chemical resistance of concrete to chloride ingress. However, for research purposes it is better to measure separate properties, as the factors that influence these two properties differ.

ingress. There is therefore a need for a suitable chloride binding test, which could be used in conjunction with a rapid chloride test to characterise the potential durability of concrete in terms of chloride ingress.

The fact that the trends observed in figure 8.17 (differences in correlation for different cement types) were not so evident in figure 8.16 can be attributed to the higher variability of D_a.

The common approach of predicting chloride levels from laboratory rapid chloride tests involves the following:

1. The laboratory results are correlated with D_a from on-site exposure tests.
2. From the correlation equation, D_a is determined for a specific chloride index value.
3. The ratio of C_x to C_s is determined from the calculated D_a value (where C_x is the chloride concentration at depth x into the concrete).
4. A suitable C_s value is chosen so that C_x can be solved.

It was shown (see Appendix, series 1 tests) that the coefficient of variation of the surface chloride level (C_s) determinations ranges from 20 - 26 %, while the coefficient of variation of $x_{0.4}$ determinations ranges from 13 - 16 % (see figure 8.20). Substituting a C_s value (Step 4) into the solution equation can therefore not be done with much confidence. This factor combined with the higher variability of D_a leads to an unacceptably high variation of this prediction procedure. Using the $x_{0.4}$ parameter eliminates a large portion of this variability.

The depth of the critical chloride level is also more easily understood by engineers, since it indicates directly how deep the reinforcing steel should be.

8.4.6 Conclusions

Rapid chloride test results (Cl^- index values) were correlated with two on-site chloride ingress parameters, D_a and $x_{0.4}$.

The best correlation was found between $x_{0.4}$ and the Cl^- index values. The better correlation

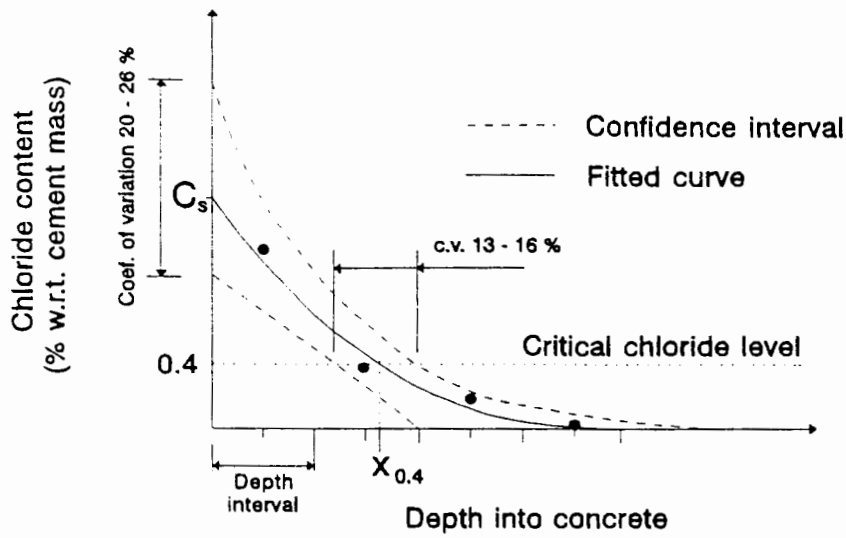

Figure 8.20 - Schematic presentation of confidence interval of a typical chloride profile

was attributed to the fact that $x_{0.4}$ is calculated from both D_a and C_s, and therefore eliminates a large portion of the scatter arising from the process of chloride profile determinations. The differences in correlations for the different cement types were ascribed to the lower chloride binding capacities of CSF concretes.

8.5 CONCLUSIONS

An analysis of chloride ingress formulae indicated that additional factors such as chloride binding, the changes in diffusivity with time and the environment should be taken into account in any chloride ingress model.

The good correlation between chloride conductivity and apparent diffusivity achieved in the series 2 tests shows promise for the development of a chloride ingress model based on the chloride conductivity test.

At this early age, the variability of the apparent chloride diffusion coefficient is still very high due to the shallow depth of chloride penetration. This factor was shown to have a substantial influence on the correlation coefficient calculated. It is suggested that the process of determining D_a and C_s be improved to reduce variability. This can be done by ensuring more representative samples are taken (eg. by using a coring or profile grinding instead of

a drilling method).

The use of an alternative chloride ingress parameter, "the depth of the critical chloride level", $x_{0,4}$, was proposed. The use of this parameter eliminates a large portion of the scatter arising from the process of chloride profile determinations. This parameter is also more easily understood by engineers, since it indicates directly how deep the reinforcing steel should be.

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CHAPTER 9

THE USE OF THE CHLORIDE CONDUCTIVITY TEST IN ENGINEERING PRACTICE

9.1 INTRODUCTION

The chloride conductivity test was developed to be used in engineering practice for:

- durability research
- predicting long-term behaviour from short-term test results
- construction quality control

This chapter describes possible applications of the test in these fields.

The series 2 tests (Appendix 2) was used to demonstrate the possibility of using the test for the purposes stated. The series 2 tests formed part of an industrial research project of which the objectives were to characterise different concretes in terms of durability-related index parameters (chloride conductivity, oxygen permeability and water sorptivity), and to correlate the index values with the performance of concrete in the field (Chapter 8). The project did not directly deal with construction quality control, however it will be shown from the results obtained that the test is sensitive to quality related parameters.

9.2 DURABILITY RESEARCH

Reinforcement corrosion resulting from chloride ingress is the greatest durability problem of reinforced concrete in marine environments. Hence, there is great need for research to provide solutions to this problem. Judging from the number of papers published in the last 10 years on durability related topics, it is evident that there is a great deal of research being conducted in this field. The characteristics of the chloride conductivity test opens new doors for durability research.

Although research is open-ended, durability research generally comprises:

1) the study of relationships between durability properties and specific factors such as:
    - cement composition
    - mix parameters
    - admixtures and additives

- treatments (curing, compaction and coatings)

2) the study of relationships between durability properties and pore structure parameters.
3) the study of the mechanisms involved in in-situ chloride ingress

There are a number of parties with an interest in durability research. Since there is a wide range of cementitious materials available today, it is vital that the users are aware of the durability related properties of these materials. It is also in the interest of the manufacturers to know the properties of the materials they produce so that these can be marketed for suitable applications. Researchers are interested in a better understanding of the material and the degradation process. Specifiers are considering the use of performance-based specifications, and are therefore looking for a measurable early-age material property which relates to the long-term performance of concrete (see section 9.3).

The chloride conductivity test is suitable for durability research because it has:

1) High precision (low inherent variability in test results relative to the range of typical test results): High precision is required so that judgements can be made with confidence.
2) Sound theoretical basis: The test measures a specific material property and not a conglomeration of properties.
3) Short test duration: When a study includes a number of factors, the possible permutations can increase dramatically. The fact that the test is simple and rapid gives the test a distinct advantage over tedious and slower tests in this respect.

Part A of Appendix 2 (series 2 tests) is an example of the use of the chloride conductivity test for durability research. The suitability of the test is reviewed on the basis of this section. Certain problems were experienced during the experimental programme. Suggestions for future similar projects are therefore made as well.

9.2.1 Review of the use of the chloride conductivity test for durability research (series 2 tests)

Figure 9.1 shows that the chloride conductivity test is sensitive to changes in w/c ratio, cement type and curing. Consistent trends can be established and there were no apparent

anomalies.

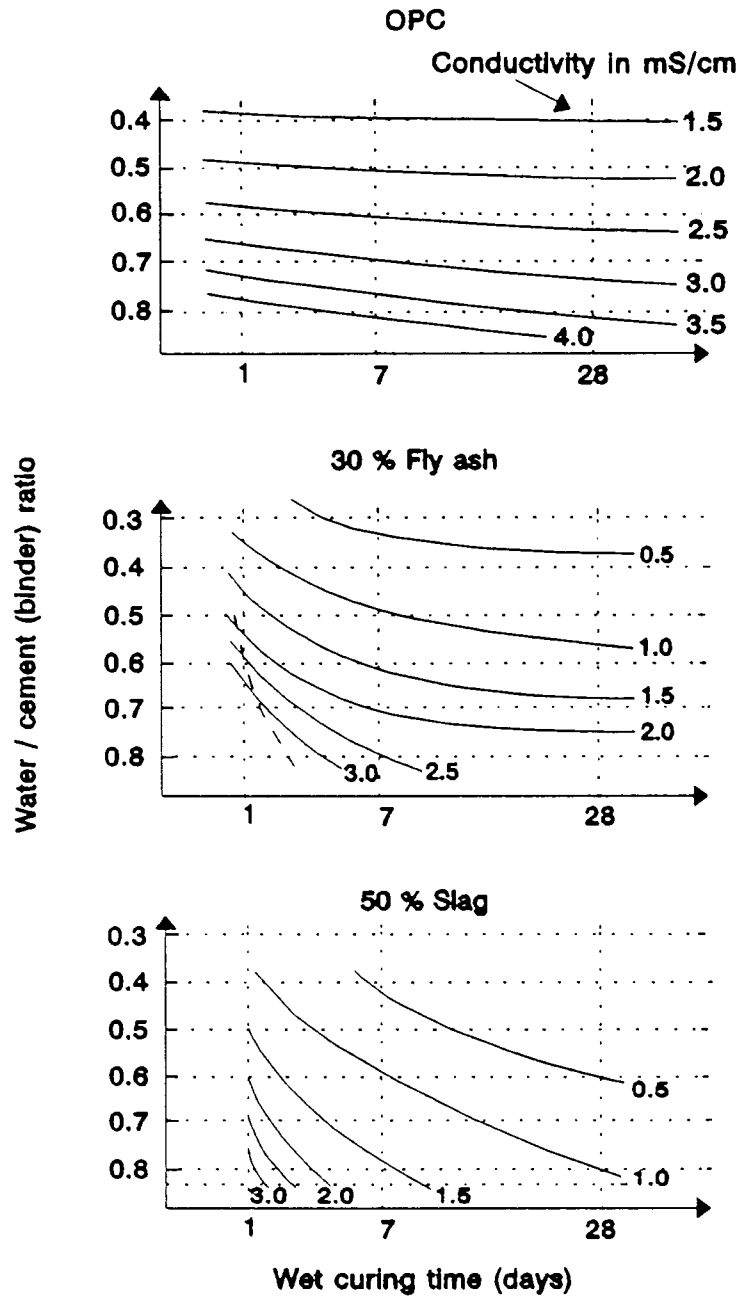

Figure 9.1: Chloride isoconductivity plots for OPC, 30 % fly ash and 50 % slag mixes.

Table 9.1 shows the range of results relative to the precision of the chloride conductivity, oxygen permeability and water sorptivity tests. The ratio of the range percentage to the precision index was substantially larger for the chloride conductivity test indicating the test to be the most sensitive to the measured property of the three tests. This factor will

dramatically increase the confidence with which judgements can be made.

Table 9.1: Range of test results relative to the precision of the chloride, permeability and sorptivity tests (series 2 tests).

	Chloride conductivity test	Oxygen permeability test	Water sorptivity test
Range of results	0.11 - 7.69 mS/cm	8.22 - 10.67 (index)	3.3 - 31.0 mm/√h
% range relative to lowest result	6890 %	29.8 %	839 %
Precision of test (1s%)	6.1 %	1.3 %	6.1 %
Ratio of % range to precision	1130	23	138

Regression analyses were performed to determine the effect of C_3A content on chloride conductivity (series 2 tests, Part A - Appendix 2). The regression analyses were found to be very useful for determining whether there is a statistically significant correlation between two variables. The method takes account of a number of factors which are omitted from precision indexes, and is hence more appropriate for the statistical analysis of data.

9.2.2 Suggestions for future projects

In the series 2 tests, surface concrete specimens were tested. This was done to determine the surface effect of curing and since the site concretes were tested in the surface region as well. If the focus was purely on the effect of cement composition and cement type on the durability related properties it would have been better to discard the as-cast concrete surface (5 - 10 mm) as this layer of concrete has a higher variability (Dhir et al, 1990; chapter 7).

Difficulty was experienced in determining the factors that caused the differences in results

between the Portland cement mixes due to the wide ranges of differences between the cements. The choice of cements is crucial if the focus is on the effect of a specific constituent in the cement. Ideally only one parameter should be changing to avoid interference. The experimental programme should be structured to facilitate the use of regression analyses.

9.3 PREDICTION OF LONG-TERM BEHAVIOUR FROM SHORT-TERM TEST RESULTS

Existing durability specifications (which prescribe mix parameters, cover depths, curing and compaction) were found to be inadequate by Mackechnie (1996) due to the dependence of durability properties on cement composition and the difficulty in testing for compliance on site. This problem is exacerbated by the increasing number of cements and mineral extenders on the market. A more rational approach using performance-based specifications was proposed: it involves specifying a measurable early-age property which relates to the long-term performance of concrete.

Diffusivity was identified as the most significant property governing the rate of chloride ingress (chapter 3). However, diffusivity could not be regarded as a measurable early-age property as diffusion tests are of too long duration. The development of the chloride conductivity test has changed this situation. The measured property "chloride conductivity" was shown to be directly related to the steady state chloride diffusion coefficient (chapter 6). It is the only chloride test that measures this property using one instantaneous measurement.

It was shown in chapter 8 that there is a good correlation between the chloride conductivity results and in-situ chloride ingress parameters verifying the potential of the test to predict chloride ingress. The test should ideally be used in conjunction with a tried and tested chloride ingress model if it is to be used for the prediction of long-term chloride ingress. Chloride ingress is an intricate process which involves a number of variables. The roles of all these variables ie. the environment, the physical and the chemical resistance of concrete to chloride ingress, and the changes in concrete properties with time need to be taken into account.

Mackechnie (1996) has developed a chloride ingress model based on the chloride conductivity test developed in this thesis.

9.3.1 Mackechnie's (1996) chloride ingress model

The Mackechnie chloride ingress model essentially involves the following elements.

1) The chloride conductivity of the relevant concrete is tested at 28 days.
2) The chloride conductivity value is adjusted to allow for chemical binding and additional hydration effects. These adjustments depend on cement type and was determined using the relative reduction in chloride conductivity from 28 days to 98 days.
3) The adjusted chloride conductivity value is converted to a 2 year apparent diffusion coefficient, $D_{a,2y}$. The conversion is based on correlation studies with 2 year in-situ tests from three exposure zones (severe, very severe and extreme).
4) An allowance is made for the reduction in apparent diffusivity with time using Mangat and Molloy's (1994) method. The reduction factor, m, is based on long-term data from Bamforth (1994) and Mackechnie (1996).
5) A suitable surface chloride concentration, C_s, is chosen based on existing data obtained from field exposure samples and marine concrete structures (Mackechnie, 1996). The surface chloride level is a function of cement type and exposure zone.
6) Using $D_{a,2y}$, C_s, and m, the chloride concentration at a specific depth and time, C_x, can be calculated using Mangat and Molloy's (1994) solution to Fick's second law.

The advantage of this model is that it takes account of all the relevant factors. It is however very difficult to determine the statistical confidence of predictions due to the many parameters involved and their interrelationships. Correlation studies in this thesis (chapter 8) proposed the combination of D_a and C_s into a new parameter $x_{0.4}$ (the depth of the critical chloride level) to reduce this problem.

Work is required on step 2 of the model. The use of adjustments based on the reduction in chloride conductivity with time is very empirical and also takes a long time (98 days). There are a number of factors causing the reduction in conductivity including chloride binding and additional hydration (see chapter 6). The use of a test that accurately measures the chloride

binding characteristics of the concrete in isolation would be preferred. From an academic point of view, the degradation process will be better understood if specific properties of the material are known. The proposed chloride binding test (chapter 6) should be developed for this purpose. This test is also likely to have a much shorter duration.

9.4 CONSTRUCTION QUALITY CONTROL

One of the most serious problems of existing durability specifications is the difficulty in testing for compliance on site. The chloride conductivity test is suitable for this purpose as it is sensitive to most of the quality related parameters:

- water/cement ratio
- cement type
- cement content
- curing
- compaction

The only quality aspect which is not dealt with is cover to reinforcement. A cover meter would be required for this purpose.

If compared with other durability index tests such as gas permeability and water sorptivity tests, the chloride conductivity test is more sensitive to w/c ratio and cement type (see Appendix 2 - Part A). Hence, for applications where these factors are important ie. where chloride corrosion is the predominant concern, the chloride conductivity test is more appropriate.

It would be unwise to wait until accurate service-life predictions can be made from durability index tests if there are gross violations of current specifications. The use of a durability index test in conjunction with a cover meter after construction would ensure compliance to specifications.

The disadvantage of the test is that it necessarily involves coring the structure due to the nature of the sample conditioning process. However, with the other durability tests developed in this research programme, coring is also required due to the advantages (in terms of precision) proper sample conditioning yields.

9.5 CONCLUSIONS

The chloride conductivity test is suitable for durability research because it has a:

- high precision
- sound theoretical basis
- short test duration.

Based on experience obtained in the series 2 tests it was suggested that the as-cast concrete surfaces of the specimens be discarded to further improve the precision of the test. Care should also be taken when selecting the materials to limit the number of variables involved. The experimental programme should also be structured in such a way so that regression analyses can be performed, as this is the only way to determine the statistical significance of correlations.

The good correlation obtained between the chloride conductivity results and in-situ chloride ingress parameters (chapter 8) verified the potential of the test to predict chloride ingress. The test should ideally be used in conjunction with a tried and tested chloride ingress model if it is to be used for the prediction of long-term chloride ingress. Chloride ingress is an intricate process which involves a number of variables. The roles of all these variables ie. the environment, the physical and the chemical resistance of concrete to chloride ingress, and the changes in concrete properties with time need to be taken into account. Mackechnie (1996) developed a chloride ingress model based on the chloride conductivity test.

The chloride conductivity test could be used for construction quality control as it is sensitive to most of the quality related parameters:

- water/cement ratio
- cement type
- cement content
- curing
- compaction

The only quality aspect which is not dealt with is cover to reinforcement. A cover meter would be required for this purpose. It would be unwise to wait until accurate service-life predictions can be made from durability index tests if there are gross violations of current specifications. The use of a durability index test in conjunction with a cover meter after

construction would ensure compliance to specifications.

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CHAPTER 10

CONCLUSION

10.1 THE NEED FOR A NEW RAPID CHLORIDE TEST

The time to initiation of chloride corrosion of reinforcement depends on the rate at which chloride ions enter concrete. Chloride ions enter concrete mainly by the mechanism of diffusion and to a lesser extent via absorption and permeation. Concrete provides resistance to chloride ingress by means of its physical pore structure and its chemical ability to bind chloride ions.

Existing durability specifications (which prescribe mix parameters, cover depths, curing and compaction) were found to be inadequate by Mackechnie (1996) due to the dependence of durability properties on cement composition and the difficulty in testing for compliance on site. A more rational approach using performance-based specifications was proposed: it involves specifying a measurable early-age property which relates to the long-term performance of concrete. Work has already been done on characterising concrete using absorption and permeability tests (Ballim, 1993).

A test that measures the diffusivity of concrete seems appropriate. However, diffusion is a very slow process, and laboratory diffusion tests are generally of too long duration to be of practical use for routine testing. A study of electrochemistry indicated that diffusivity could be determined using conductivity measurements.

All existing rapid chloride tests are conduction tests, with negligible diffusion taking place. However, these tests were shown to suffer from serious problems:

- Whiting's (1981) test is severely influenced by the porewater conductivity of the concrete which is irrelevant to the physical resistance of concrete to chloride ingress.
- The Dundee rapid chloride test (Dhir et al, 1990) is of too long duration.

The need for the development of a new rapid chloride test which measures the physical resistance (diffusivity) of concrete to chloride ingress was identified.

10.2 THE RAPID CHLORIDE CONDUCTIVITY TEST

A test that measures the physical resistance of concrete to the transport of chloride ions was developed. The main advantages of the test in relation to existing test methods are presented below:

- As far as can be ascertained, the test is the most rapid of all chloride tests developed to date. It is the only test that measures the physical resistance of concrete to chloride ingress using one single measurement after sample conditioning.
- The test has a sound theoretical basis and measures the required property in the absence of outside influences. The use of the high concentration chloride solution (5 M NaCl) to saturate the concrete specimens ensures the standardisation of the concrete pore solution conductivity, hence the conductivity measurement of the specimen is directly related to the steady state chloride diffusivity of the concrete.
- The test is of low cost, and is easy to use. The test apparatus uses a silicone rubber collar which mechanically clamps the concrete specimens to allow rapid changeover from one sample to another.
- The test method was standardised with the use of a ruggedness test (ASTM E 1169-89). The test is sufficiently rugged to withstand small changes in the operating conditions of the test.
- The test has a high precision and is very sensitive to the measured property. The single-operator coefficient of variation of the test was estimated to be 6 % (where 3 test determinations constitute a test result) while the range of test results spans approximately 2 orders of magnitude.

An extensive laboratory- and site based experimental programme was carried out to demonstrate the possibility of using the test in engineering practice.

10.3 THE USE OF THE CHLORIDE CONDUCTIVITY TEST IN ENGINEERING PRACTICE

10.3.1 Durability research

The chloride conductivity test is ideally suited for durability research because of its:

- high precision: High precision is required so that judgements can be made with confidence.
- sound theoretical basis: For research purposes, a test that measures a specific property is preferred to facilitate a better understanding of the processes involved.
- short test duration: When the number of variables tested is increased, the possible permutations can increase dramatically, hence a simple rapid test will have a distinct advantage over a tedious slower test.

10.3.2 Prediction of long-term chloride ingress

Existing prescriptive durability specifications were found to be inadequate due to the dependence of durability properties on cement composition and the difficulty in testing for compliance on site. This problem is exacerbated by increasing number of cements and mineral extenders on the market which were shown to differ substantially in durability properties (see Appendix 2, series 2 tests). A more rational approach using performance-based specifications was proposed: it involves specifying a measurable early-age property which relates to the long-term performance of concrete. Reliable predictions of chloride ingress based on the chloride conductivity test will support this approach.

Chloride ingress is a complicated process involving a number of factors:

- The physical resistance of concrete to chloride ingress.
- The chemical resistance of concrete to chloride ingress (chloride binding).
- The change in material properties with time.
- The severity of the exposure conditions (environment).

The chloride conductivity test should therefore be included in a chloride ingress model if it is to be used to predict long-term chloride ingress. Mackechnie (1996) developed such a

model based on the use of the chloride conductivity test, using correlation studies and existing data. This model takes account of all the relevant factors. At this stage it is still difficult to determine with what confidence predictions can be made, however correlation studies performed in this thesis displayed considerable promise.

10.3.3 Construction quality control

The test was shown to be sensitive to most of the quality related parameters:

- w/c ratio
- cement type
- cement content
- curing
- compaction

The test could therefore effectively be used as a construction quality control test purely on this basis.

10.4 FUTURE RESEARCH

10.4.1 Chloride binding

The chloride conduction test determines mainly the physical resistance of concrete to chloride ingress. Chloride ingress on-site (non-steady state chloride diffusion) is strongly influenced by the chemical resistance (chloride binding effects) of concrete to chloride ingress. Current tests which measure the chloride binding characteristics of concrete require expensive and specialist equipment and are not suitable for routine laboratory tests. The need for a suitable laboratory test that characterises the chemical resistance of concrete to chloride ingress was identified.

In the chloride ingress model developed by Mackechnie (1996), the chemical resistance of concrete to chloride ingress was assessed with the reduction in chloride conductivity after 98

days immersion in a 5 M NaCl solution. At this high concentration the test is not that sensitive to a reduction in chloride concentration in the pore solution. It was shown that when a lower concentration (3 M NaCl) solution is used, the test becomes very sensitive to any reduction in the chloride concentration in the pore solution.

A rapid chloride binding test was proposed which measures the reduction in conductivity of a concrete sample saturated with a suitable (0.5 - 3 M) chloride solution. The test can easily be verified with pore expression tests.

10.4.2 Long-term chloride ingress

Since concrete properties change with time, the on-site exposure tests should be continued so that these effects can be studied. Most of the high strength mixes (60 and 75 MPa) had very small depths of chloride penetration and could not be analyzed accurately at early ages (1 and 2 years).

Future correlation studies can be used to refine the existing chloride ingress model, and will improve the confidence with which chloride ingress can be predicted.

Appendix 1 deals with the series 1 tests. This series of tests formed part of an industrial research project. The experimental methods of this project and the correlation study are included in the main body of the thesis. The discussion of laboratory test results is included in this appendix since the objectives of the industrial research project were different to that of this thesis. The correlation study between the chloride index values and the in-situ chloride ingress is included in chapter 8.

The industrial research project had the following scope and objectives:

> The objective was to determine the effect CSF has on the resistance of concrete to chloride ingress. Two types of CSF (undensified and densified) at different replacement levels (0, 5 and 10 %), different target strengths (25, 50 and 75 MPa), and different curing regimes (1, 7 and 28 day wet curing) were used in the laboratory tests.

Contents of Appendix 1:

Part A: Discussion of laboratory test results.

Part B: Figures and tables.

PART A

1. Discussion of chloride index test results

The chloride index values (in mA), for each concrete sample tested, are displayed in table 2. A summary of these results (averaged) is displayed with those of the other tests in table 1. Three samples from different cubes for each mix with the same curing regime were tested.

An increase in concrete strength greatly reduced the chloride index values for all the mixes. The chloride index values were also lower for the concrete samples that had been moist cured for longer periods. The improvement was generally more evident from 1 to 7 days moist curing than from 7 to 28 days moist curing. See figures 1, 2 and 3:

The addition of silica fume reduced the chloride index values for all mixes, with the sole

exception of the 25 MPa, 1 day moist cured samples (except 5 % UCSF). The results also indicated that the improvement with curing was more pronounced with the silica fume concretes, ie. these concretes were more sensitive to poor curing. The use of UCSF reduced the chloride index more than DCSF, for the 50 MPa and 75 MPa concretes. Note that the 75 MPa 5 % UCSF mix included a superplasticizer and the 75 MPa 5 % DCSF mix did not. The superplasticizer might well have dispersed the silica fume more efficiently, explaining this improvement. The use of 10 % CSF reduced the chloride index more than using 5 % CSF (50 MPa mixes), for both the UCSF and the DCSF. See figures 4, 5 and 6.

Chloride "isopermeability" lines were also plotted for both the 5 % UCSF and 5 % DCSF mixes, compared with the OPC control mixes (see figures 7 and 8). These graphs give an indication of what mix and curing time would be required to achieve a certain chloride index level. The steeper lines for the silica fume mixes (dotted lines) indicate their increased sensitivity with respect to curing. The improvement effected by csf is clearly indicated by the silica fume lines lying below the OPC lines on the graphs. The 5 % UCSF mixes performed better than the 5 % DCSF mixes especially at the higher strengths (note that the 5 % UCSF 75 MPa mix included a superplasticizer) and shorter required moist curing times. The 5 % DCSF continued improving from 7 to 28 days indicating a slower rate of microstructure improvement (or chloride permeability reduction) compared with the equivalent UCSF mix. (The pozzolanic reaction increases the tortuosity of the pores thus reducing the diffusibility of the material.)

2. Conclusions

2.1 The use of CSF improved the chloride index values, especially for 50 MPa and 75 MPa mixes compared with OPC. The 10 % replacement mixes had lower chloride index values compared with the 5 % replacement mixes. An increase in strength improved the chloride index values for all the mixes.

2. UCSF performed slightly better than DCSF in the chloride index tests. The chloride index tests showed that the UCSF mixes were more sensitive to curing at the very early ages (1 - 7 days wet curing) compared with OPC, and the DCSF mixes were more sensitive to curing at the early (1 - 7 days wet curing) and the later (7 - 28

days) ages compared with OPC. This indicated a slower reaction rate for the DCSF mixes.

3. The use of a superplasticizer seemed to improve the performance of the 75 MPa 5 % UCSF mix over the 75 MPa 5 % DCSF mix in terms of the chloride index test. Note that the chloride index test measures mainly the physical resistance of concrete to chloride ingress.

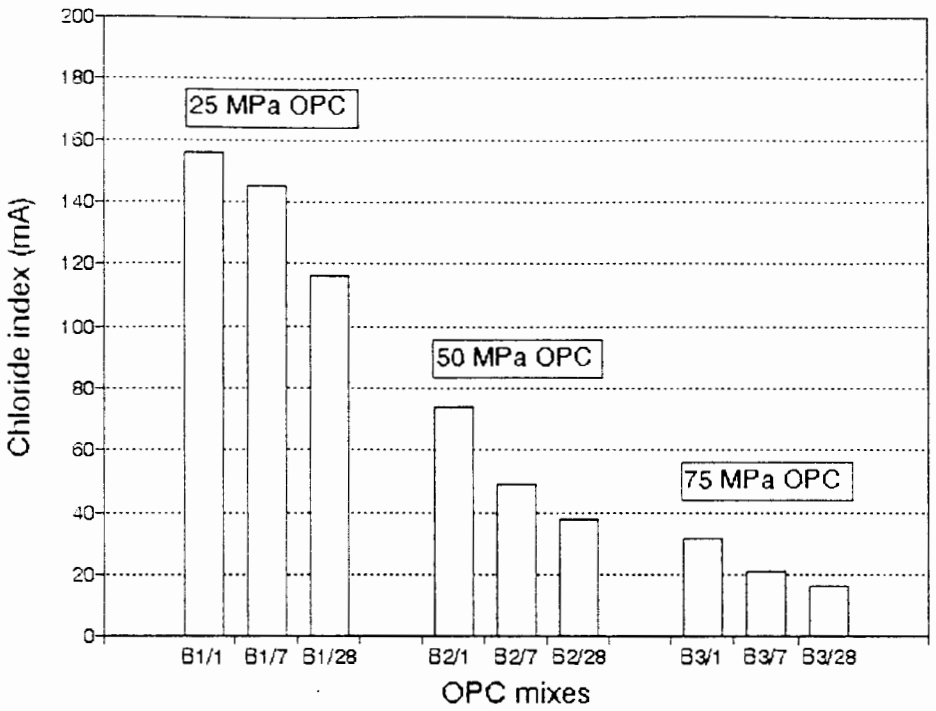

Figure 1: Chloride index results: OPC mixes.

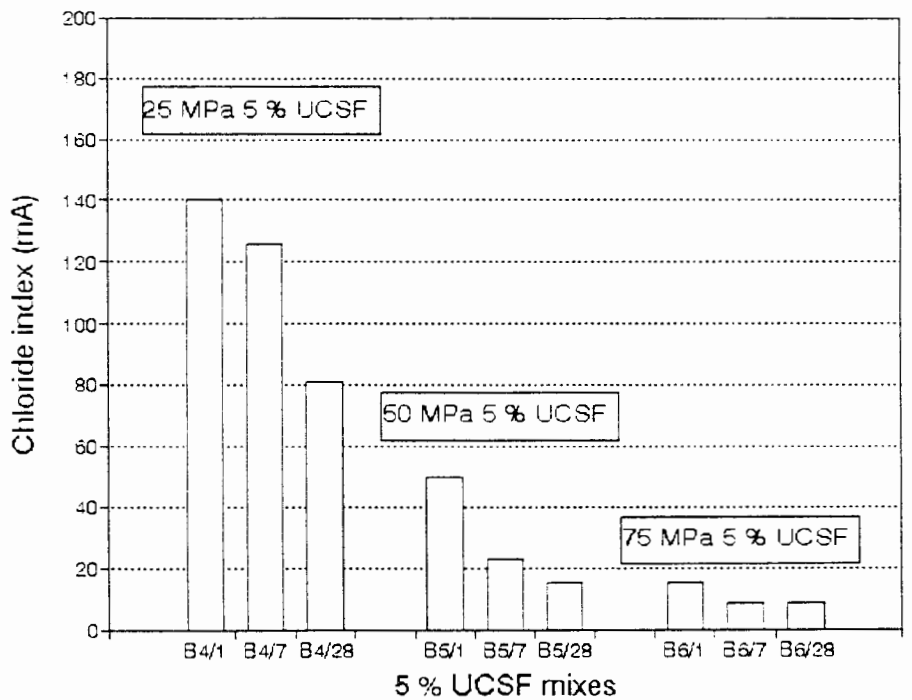

Figure 2: Chloride index results: 5 % UCSF mixes.

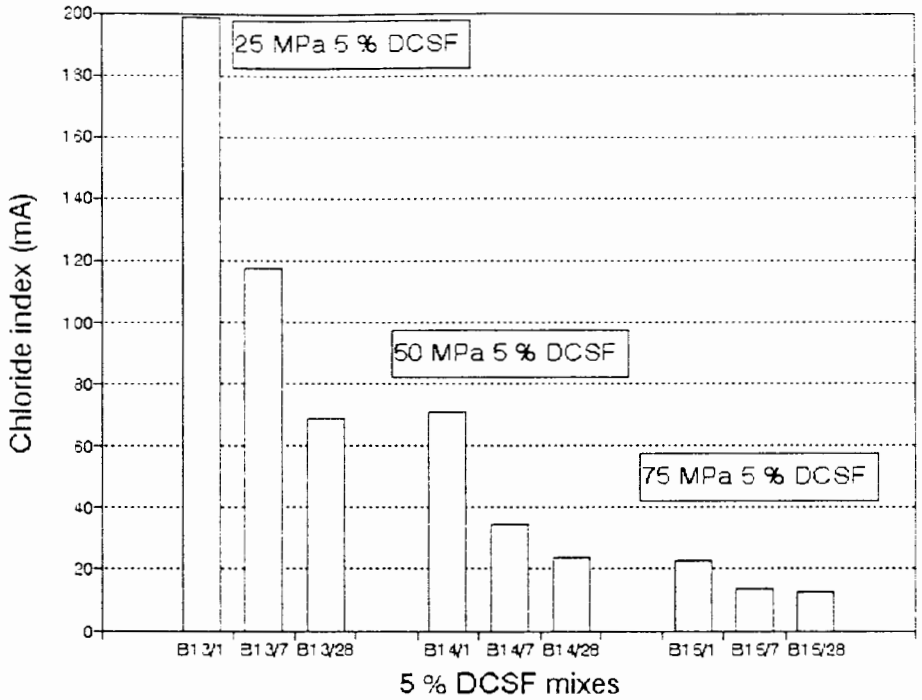

Figure 3: Chloride index results: 5 % DCSF mixes.

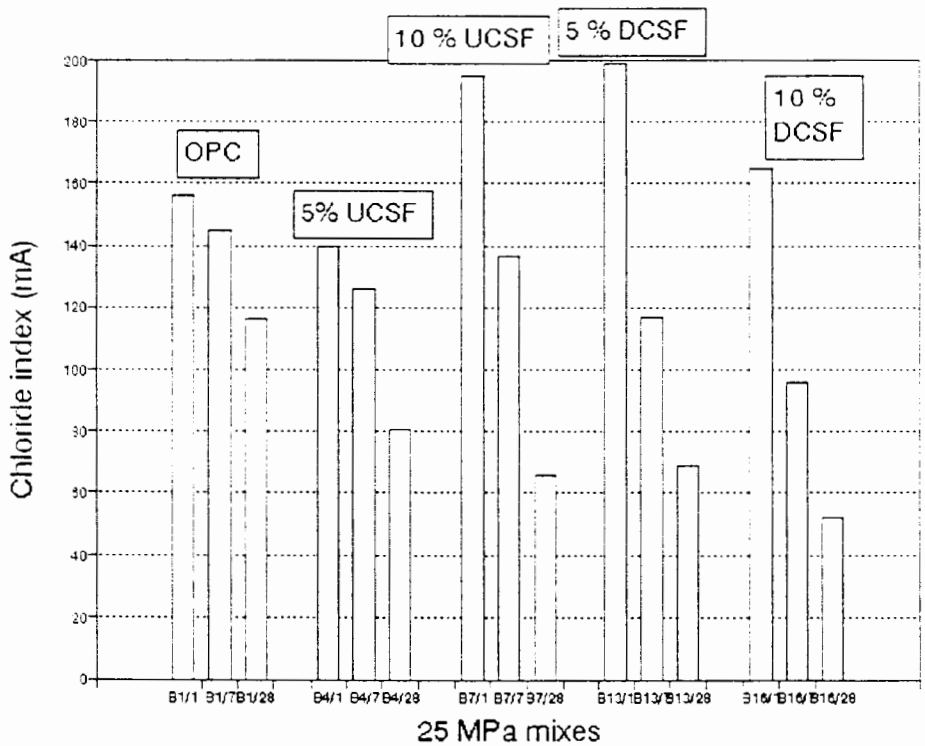

Figure 4: Chloride index results: 25 MPa mixes.

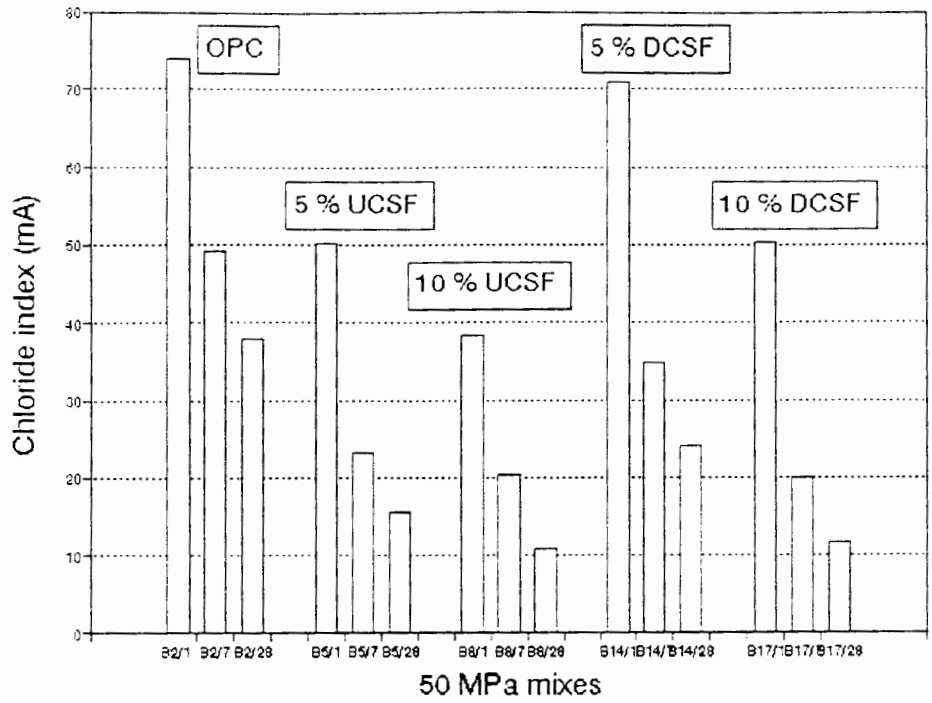

Figure 5: Chloride index results: 50 MPa mixes.

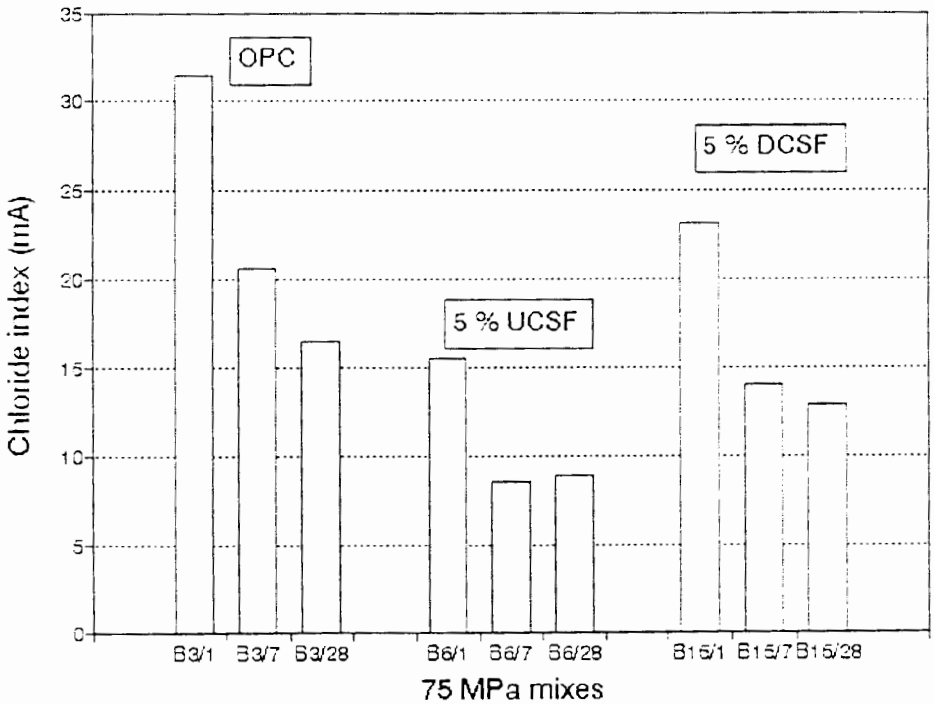

Figure 6: Chloride index results: 75 MPa mixes.

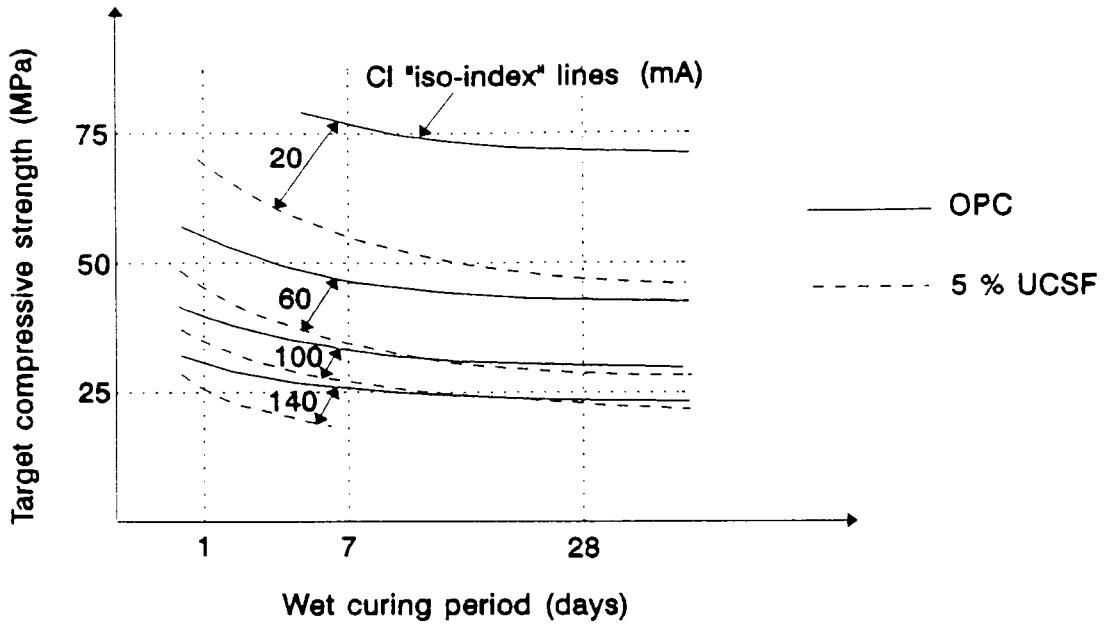

Figure 7: Chloride "iso-index" lines: OPC and 5 % UCSF mixes.

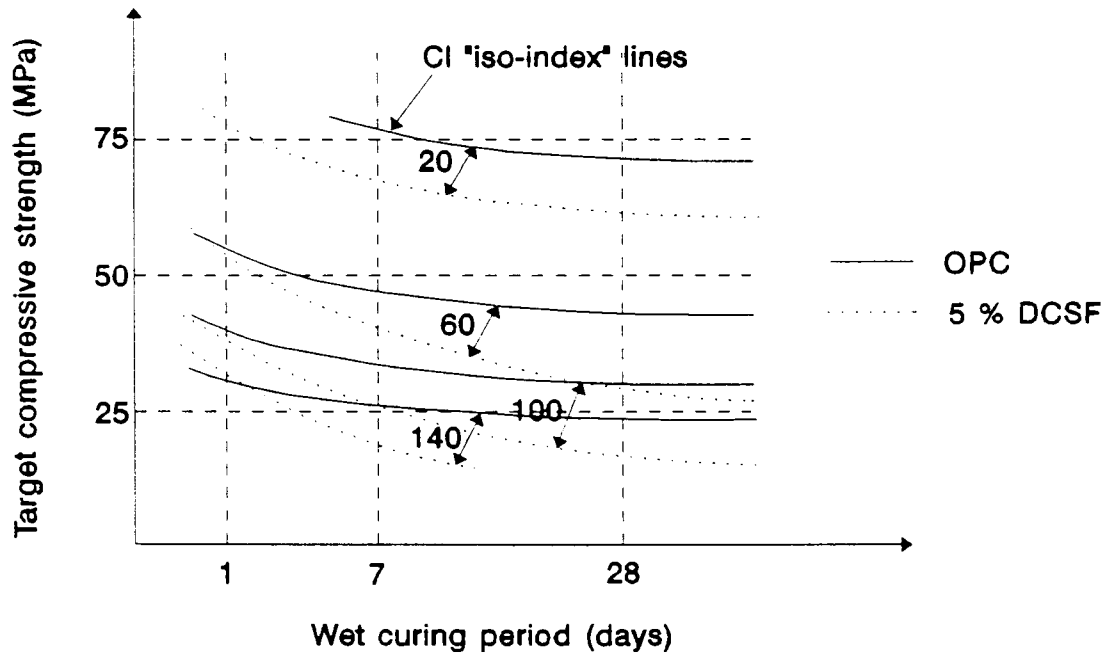

Figure 8: Chloride "iso-index" graph: OPC and 5 % DCSF mixes.

Table 1: Summary of UCT experimental results (mean values).

Mix	Mix no.	Sorptivity (mm/√hr)	Permeability index	Chloride index (mA)
OPC 25 MPa	B1/1	20.9	8.80	156
	B1/7	11.7	9.37	145
	B1/28	11.0	10.09	116
OPC 50 MPa	B2/1	16.8	9.45	74.3
	B2/7	14.6	10.00	48.7
	B2/28	9.90	10.36	38.0
OPC 75 MPa	B3/1	11.4	9.69	31.5
	B3/7	11.3	10.03	20.6
	B3/28	12.5	10.21	16.5
UCSF 5% 25 MPa	B4/1	23.1	9.00	140
	B4/7	13.1	9.56	126
	B4/28	9.57	9.86	80.7
UCSF 5% 50 MPa	B5/1	10.5	9.49	50.1
	B5/7	8.59	9.90	23.3
	B5/28	5.47	10.08	15.5
UCSF 5% 75 MPa	B6/1	10.4	9.76	15.5
	B6/7	8.96	10.31	8.60
	B6/28	7.46	10.61	8.90
UCSF 10% 25 MPa	B7/1		8.87	195
	B7/7	17.5	9.02	137
	B7/28		9.32	66.2
UCSF 10 % 50 MPa	B8/1	12.3	9.36	38.3
	B8/7	7.74	9.64	20.4
	B8/28	6.62	9.76	10.9
UCSF 10 % 75 MPa	B9/28	8.76	10.80	
UCSF 15% 25 MPa	B10/28	9.79	9.28	Mixes not
UCSF 15% 50 MPa	B11/28		9.66	tested
UCSF 15% 75 MPa	B12/28		9.99	
DCSF 5% 25 MPa	B13/1	19.1	8.90	199
	B13/7	14.8	9.46	117
	B13/28	8.61	10.00	69.4
DCSF 5 % 50 MPa	B14/1	12.9	9.17	70.8
	B14/7	10.3	9.75	34.8
	B14/28	9.21	9.96	24.1
DCSF 5 % 75 MPa	B15/1	11.6	9.41	23.1
	B15/7	7.66	9.90	14.0
	B15/28	7.02	10.01	12.8

table 1 - continued

Mix	Mix no.	Sorptivity (mm/√hr)	Permeability index	Chloride index (mA)
DCSF 10% 25 MPa	B16/1	20.6	9.05	165
	B16/7	14.8	9.25	95.8
	B16/28	9.71	9.56	51.9
DCSF 10% 50 MPa	B17/1	14.9	9.17	50.3
	B17/7	6.66	9.61	20.0
	B17/28	6.23	9.76	11.5
DCSF 10% 75 MPa	B18/28	5.04	10.43	Mixes not tested
DCSF 15% 25 MPa	B19/28		9.20	
DCSF 15% 50 MPa	B20/28	6.51		
DCSF 15% 75 MPa	B21/28	6.52	10.02	

Table 2: Chloride index test results.

Mix	Chloride index (mA)	Average (mA)	Standard deviation (mA)	Coefficient of variation (%)
B1/1	144 160 165	156	8.96	5.73%
B1/7	133 162 140	145	12.4	8.52%
B1/28	117 122 108	115	5.79	5.01%
B2/1	69.8 76.5 76.5	74.3	3.16	4.25%
B2/7	46.2 55.1 44.8	48.7	4.56	9.37%
B2/28	30.7 42.6 40.6	38.0	5.20	13.7%
B3/1	30.2 31.4 32.8	31.5	1.06	3.38%
B3/7	19.8 20.9 21.0	20.6	0.540	2.64%
B3/28	15.2 18.3 15.9	16.5	1.33	8.06%
B4/1	147 134 139	140	5.35	3.82%
B4/7	129 122	125		
B4/28	68.0 108 66.0	80.7	19.3	24.0%
B5/1	55.3 45.5 49.6	50.1	4.02	8.02%

table 2 - continued

Mix	Chloride index (mA)	Average (mA)	Standard deviation (mA)	Coefficient of variation (%)
B5/7	25.3 23.9 20.6	23.3	1.97	8.47%
B5/28	15.7 15.1 16.7	15.8	0.690	4.37%
B6/1	12.4 18.5 15.5	15.5	2.49	16.1%
B6/7	7.30 7.70 10.9	8.60	1.61	18.7%
B6/28	10.2 7.60	8.90		
B7/1	208 181	195		
B7/7	148 140 124	137	9.70	7.06%
B7/28	50.5 68.8 79.3	66.2	11.9	18.0%
B8/1	53.6 37.0 24.2	38.3	12.1	31.5%
B8/7	20.9 17.3 22.9	20.4	2.30	11.3%
B8/28	10.7 9.33 12.8	10.9	1.41	12.9%
B13/1	207 190	199		
B13/7	115 116 119	116.6	1.65	1.42%

table 2 - continued

Mix	Chloride index (mA)	Average (mA)	Standard deviation (mA)	Coefficient of variation (%)
B13/28	77.8 73.0 57.3	69.4	8.75	12.6%
B14/1	61.4 76.2 74.9	70.8	6.69	9.45%
B14/7	33.7 33.4 37.4	34.8	1.82	5.22%
B14/28	28.0 17.4 27.0	24.1	4.79	19.9%
B15/1	24.5 24.8 20.1	23.1	2.17	9.37%
B15/7	12.9 14.3 14.7	14.0	0.740	5.28%
B15/28	14.0 12.1 12.4	12.8	0.840	6.51%
B16/1	171 159	165		
B16/7	79.5 106 101	95.8	11.7	12.2%
B16/28	36.3 68.1 51.3	51.9	13.0	25.0%
B17/1	54.4 49.4 47.1	50.3	3.05	6.06%
B17/7	23.0 21.0 16.0	20.0	2.93	14.6%

table 2 - continued

Mix	Chloride index (mA)	Average (mA)	Standard deviation (mA)	Coefficient of variation (%)
B17/28	12.6 10.0 12.0	11.5	1.12	9.69%

Appendix 2 deals with the series 2 tests. This series of tests formed part of an industrial research project. The experimental methods and the correlation study of this project are included in the main body of the thesis (chapters 4 and 8 respectively). The discussion of the chloride conductivity test results is included in this appendix since the objectives of the industrial research project were different to that of this thesis. This work is related to this thesis since it is an example of the use of the test in engineering practice (see chapter 9).

The industrial research project had the following scope and objectives:

Different concretes were to be characterised in terms of durability-related index parameters. The intention was to correlate the characterisation index values with the performance of concrete in the field.

The focus was on the influence that C_3A levels, Alite/Belite ratios and the addition of mineral extenders (fly ash and slag) have on the durability of concrete, in particular marine durability in terms of chloride ingress.

Three durability characterisation tests: chloride conductivity, oxygen permeability and water sorptivity, were selected to characterise the potential durability of the material so that its performance could be predicted over a range of aggressive environments. A full scope of mixes (20, 40 and 60 MPa) and curing regimes (1, 7 and 28 days wet curing) were used for the characterisation tests.

Note: Only the chloride conductivity results are discussed in this appendix. Correlations between the other index tests and in-situ chloride tests are dealt with in chapter 8.

Contents of Appendix 2

PART A

1 Cube compression tests

Three cubes were crushed from each type of concrete after 3, 7, 28 and 90 days wet curing. The three compressive strength determinations were averaged to obtain one cube test result. All the cube test results are included in Part B - table 1.

1.1 Below strength mixes

Some mixes did not achieve the prescribed 28 day target strengths (see table 1). Of the 31 mixes, 10 were below strength by more than 5 %. Of these, 4 mixes were below strength by more than 15 % (mixes 4, 11, 13 and 28).

The actual strengths of all the other mixes were within 5 % of the target strengths.

The reason for the low strengths of most of these mixes can be ascribed to a too high w/c ratio, and not because of contamination or mixing errors. All the 40 MPa slag mixes (marked with a '#' in table 1) were below strength, and averaged around 34 MPa. It is very unlikely that similar errors were made during mixing with all these mixes, and more likely that the w/c ratio used for these mixes was incorrect.

In this chapter, comparisons which include the blended mixes are based on w/c and not strengths, and therefore obviate this problem. With the 40 MPa target strength Portland cement mixes which were below strength (mixes 5, 13 and 14), the durability index test values where adjusted to those of equivalent 40 MPa mixes and to equivalent 0.56 w/c ratio mixes. This was done by interpolating between the 20, 40 and 60 MPa target strength mixes.

It is clear that the below strength mixes did not leave large gaps in the data.

Table 1: Mixes which did not achieve the prescribed target strengths.

Mix number	Cement type	28 day actual strength (MPa)	28 day target strength (MPa)	Percentage below strength (%)
4	De Hoek OPC	15.1	20	24.5
5		34.8	40	13.0
11	LASRC	50.6	60	15.7
13	Riebeeck West OPC	33.0	40	17.5
14		35.3	40	11.8
26	50 % slag blend with Riebeeck West OPC	34.1#	40	14.8
28	50 % slag blend with De Hoek OPC	31.9#	40	20.3
29	70 % slag blend with De Hoek OPC	36.2#	40	9.5
35	70 % slag blend with Riebeeck West OPC	36.1#	40	9.8
36		54.9	60	8.5

1.2 Strengths of the Portland cement mixes

The 28 day cube strengths of the Portland cement mixes (plotted against w/c ratio) are compared in figure 1. The points at 40 MPa represent the average of the two mixes which contained different coarse aggregates (ie. mix numbers 2 and 3, 5 and 6, 9 and 10, and 13 and 14). Note that there was no 60 MPa Slurry mix, and that the 60 MPa LASRC mix (no. 11) appeared porous and unrepresentative and was discarded.

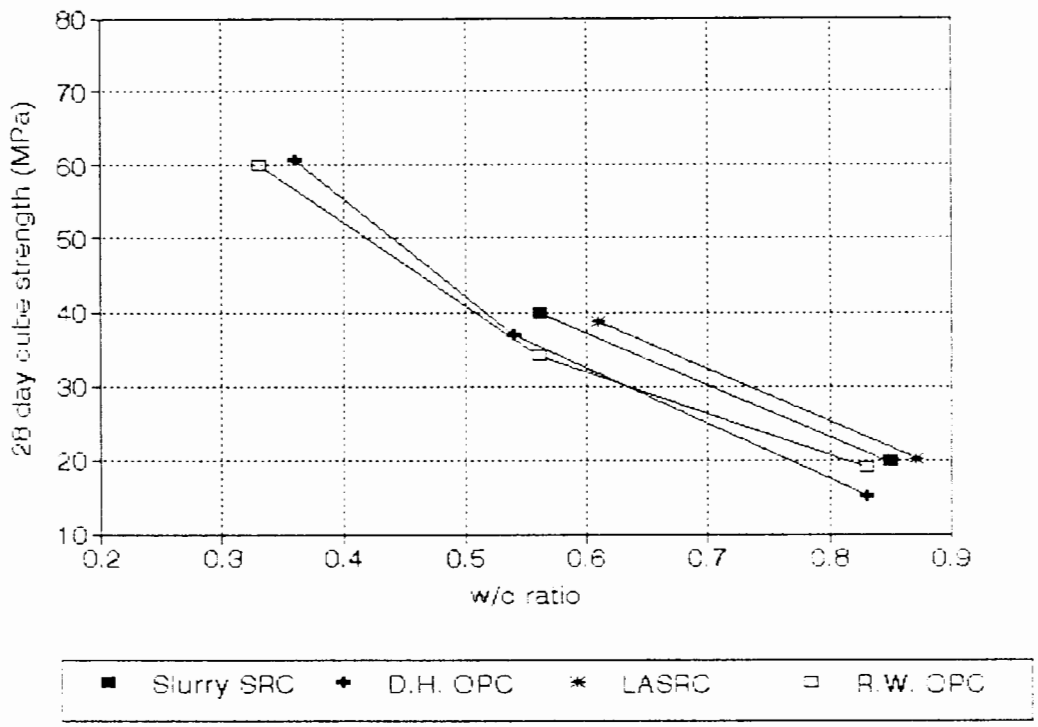

Figure 1: 28 day cube strengths of the Portland cement mixes plotted against w/c ratio.

The differences between the two OPC mixes (De Hoek and Riebeeck West) were generally small. The Slurry SRC mixes had appreciably higher strengths at equivalent w/c ratios compared with the OPC mixes, and the LASRC mixes had even higher strengths at equivalent w/c ratios. LASRC had a substantially higher Alite/Belite ratio compared with the OPC cements (4.2 vs. 2.6), which would contribute to explain the higher strengths of the LASRC mixes. The Slurry SRC had a substantially higher specific surface area compared with the OPC cements (4500 vs. 2800 cm^2/G), which would contribute to explain the higher strengths of the Slurry SRC mixes.

A graph was plotted to compare the rates of strength increase of the 40 MPa mixes made

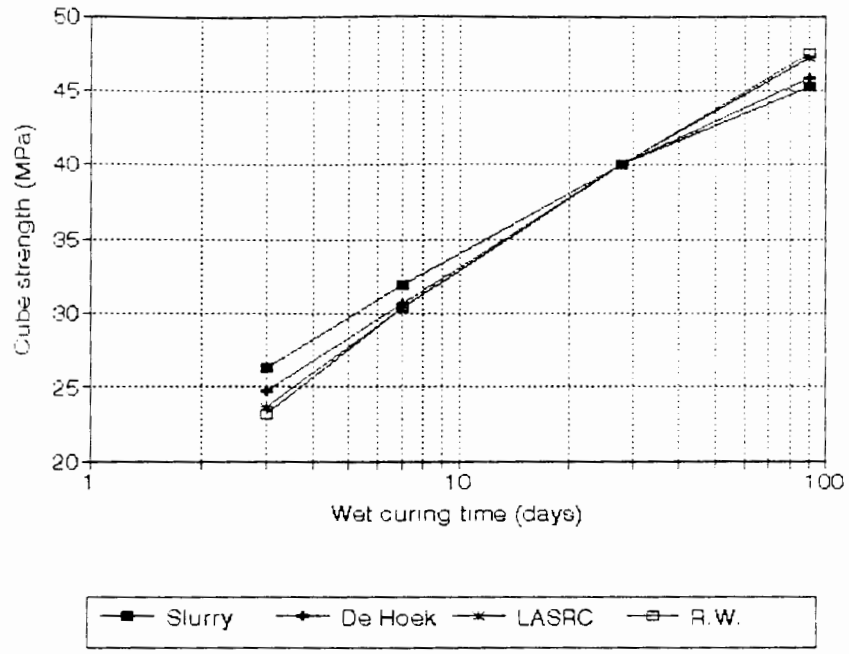

Figure 2: Cube strengths of the 40 MPa Portland cement mixes plotted against wet curing time.

with the four Portland cements (see figure 2). The results of the mixes were normalised so that all the lines passed through the target strength at 28 days (40 MPa). The strengths at all other ages were multiplied by the same factor that was used to adjust the 28 day strengths. The purpose of this graph was therefore purely to compare the rates of strength increase of the various mixes.

The differences in rates of strength gain were generally small, but the following trends were observed: The Slurry SRC mix had the highest relative strengths at early ages, and the lowest relative strengths at later ages while the LASRC mix had the lowest relative strengths at early ages, and the highest relative strengths at later ages. The higher specific surface area of the Slurry SRC cement would again contribute to explain this difference.

From the small differences in rates of strength gain, it can be inferred that the differences in rates of hydration were small. This meant that in the case of the Portland cement mixes the effects of various factors on durability properties, such as C_3A content and Alite/Belite ratios, could be collated from different curing regimes to increase the sample size for analysis purposes.

1.3 OPC vs. blended cements

The 28 day cube strengths of the 30 % fly ash, mixes 16, 17 and 18, and the 50 % slag, mixes 25, 26 and 27, mixes (blended with Riebeeck West OPC) plotted against w/c ratio (c refers to total binder content), are compared with the Riebeeck West OPC mixes (mixes 12 - 15) in figure 3. Riebeeck West OPC was chosen as the control since the blends were with Riebeeck West OPC.

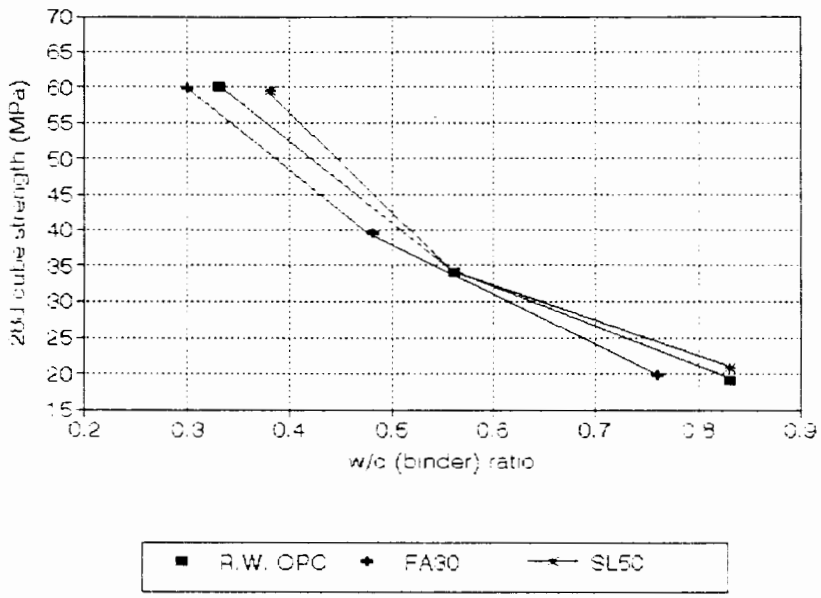

Figure 3: 28 day cube strengths of the Riebeeck West OPC, 30 % fly ash and 50 % slag blend mixes plotted against w/c (binder) ratio.

The 50 % slag blends required similar w/c ratios to achieve 20 and 40 MPa, but 12 % higher w/c ratios to achieve 60 MPa compared with the Riebeeck West OPC mixes. The 30 % fly ash mixes generally required 10 % lower w/c ratios to achieve similar target strengths as the Riebeeck West OPC mixes.

The 28 day cube strengths of the 50 % fly ash and the 70 % slag mixes (blended with Riebeeck West OPC) plotted against w/c ratio, are compared with the Riebeeck West OPC mixes in figure 4.

Both the high replacement blends needed approximately 25 % lower w/c ratios to achieve similar target strengths as the Riebeeck West OPC mixes.

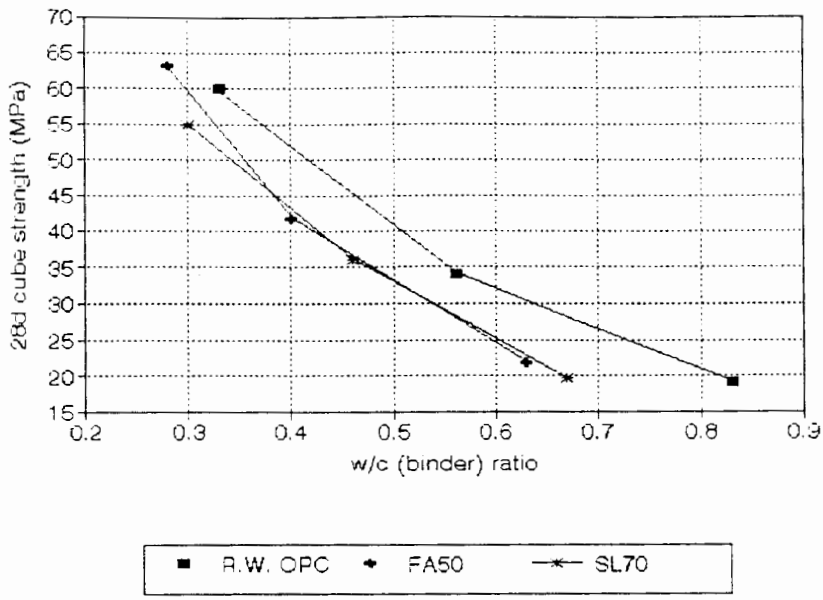

Figure 4: 28 day cube strengths of the Riebeeck West OPC, 50 % fly ash and 70 % slag blend mixes plotted against w/c ratio.

The durability index test results of the blended and the OPC mixes were compared on the basis of w/c ratio. Should the results have been compared on the basis of strength, the blends would have seemed to perform even better relative to the OPC mixes since these mixes generally required lower w/c ratios to achieve similar strengths. This is an important aspect which needs to be borne in mind when looking at work done by other researchers.

Graphs were plotted to compare the rates of strength increase of the blended cement mixes with those of the OPC mixes. The results of the OPC mixes were averaged.

As before, the results of the mixes were normalised so that all the lines passed through the target strengths at 28 days (20, 40 or 60 MPa). The purpose of these graphs was therefore purely to compare the rates of strength increase of the various mixes.

Figures 5 - 8 indicate that the blended cement mixes had slower rates of strength increase over the first 28 days compared with the OPC mixes, but higher rates of strength gain thereafter.

The slag mixes had lower strengths at 3 and 7 days compared with the fly ash mixes, indicating an even slower rate of strength increase initially. However, from 28 days to 90 days both blends generally had similar rates of strength increase.

The higher replacement mixes (figures 7 and 8) generally showed similar trends. The only consistent difference was that the 90 day strengths of the 70 % slag mixes were not higher compared with those of the OPC mixes.

The higher strengths of the blended mixes at later ages are important in the case of durability since degradation is a long term process. It is important to look not only at the absolute values of the durability index tests, but also at how these properties change with time.

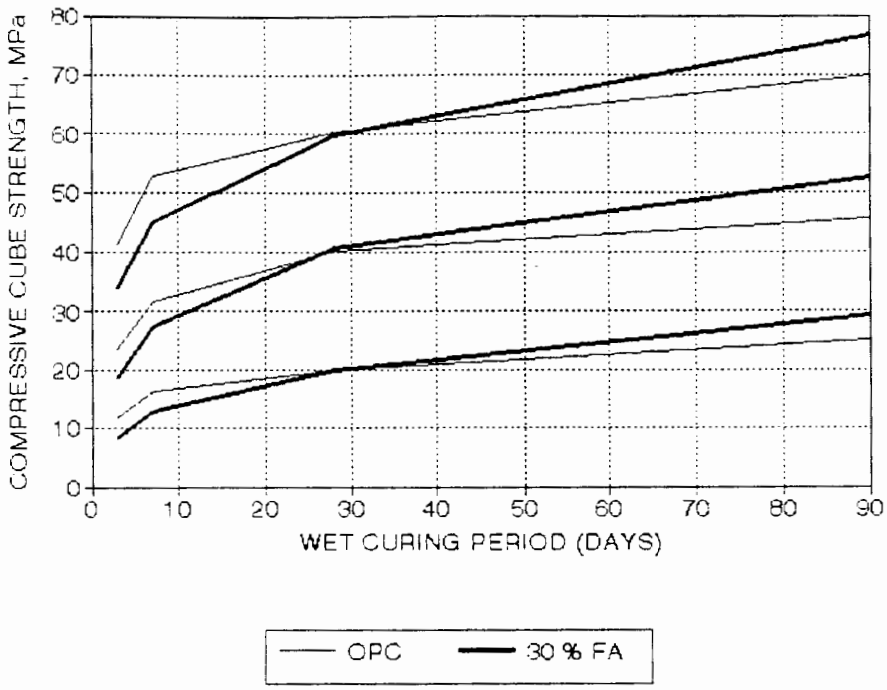

Figure 5: Normalised strength gain curves: OPC and 30 % FA mixes.

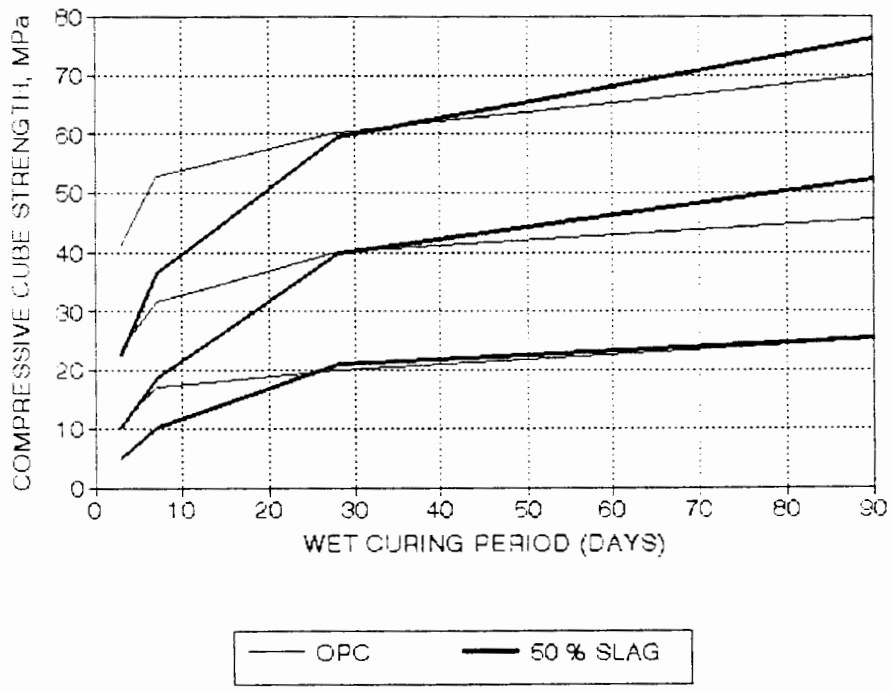

Figure 6: Normalised strength gain curves: OPC and 50 % slag mixes.

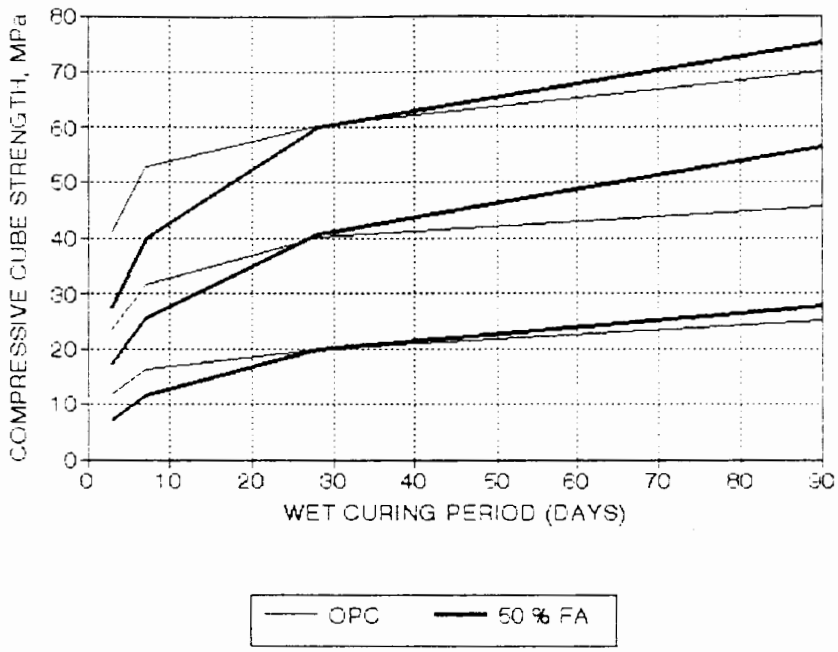

Figure 7: Normalised strength gain curves: OPC and 50 % FA mixes.

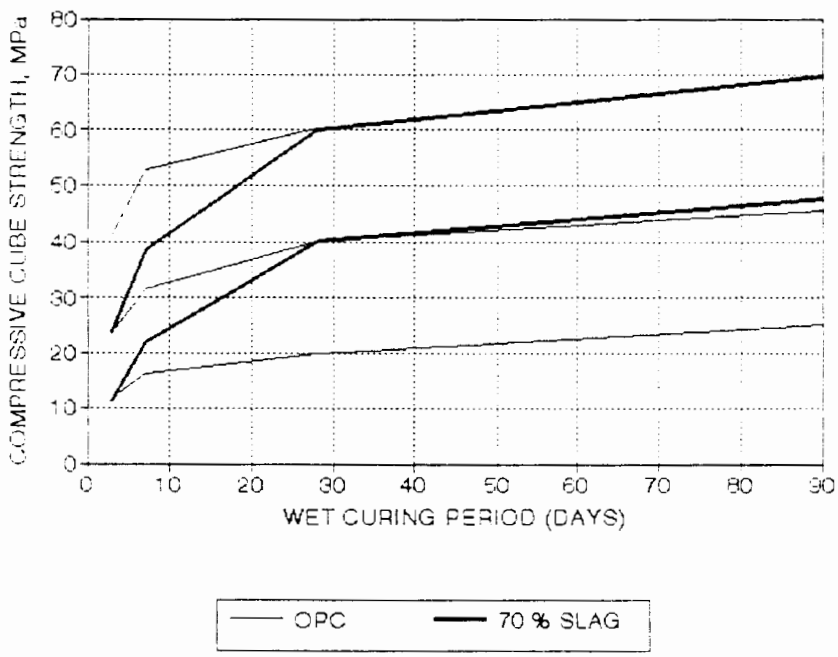

Figure 8: Normalised strength gain curves: OPC and 70 % slag mixes.

2 Chloride conductivity tests

Conductivity determinations for each type of concrete were made from three concrete specimens. The three determinations were averaged to obtain one test result for each type of concrete. The chloride conductivity test results (excluding the initial and 2 week chloride conductivity test results) are displayed with those of the other tests in Part B - table 2. The initial conductivity, chloride conductivity and 2 week chloride conductivity determinations of all the concrete specimens tested are displayed in Part B - table 3.

The single-operator coefficient of variation (1s%) of the chloride conductivity test was 7.9 % for mixes 1 - 11 and 5.8 % for mixes 12 - 36 (see chapter 7). The different values of 1s% are a result of the fact that a different operator was used after mix 12. Two test results would have to differ by more than 22 % (M1-11) and 16 % (M12-36) to be significantly different, and the acceptable range of three test determinations is 45 % (M1-11) and 33 % (M12-36) under the 95 % significance level.

2.1 Greywacke vs. granite coarse aggregates

Two 40 MPa mixes, one with greywacke coarse aggregate and the other with granite coarse aggregate were made with each of the four Portland cement types, Slurry SRC, De Hoek OPC, LASRC and Riebeeck West OPC (excluding the blended cements). The chloride conductivity test results were analyzed to see whether the use of different coarse aggregates caused any significant differences.

The differences in chloride conductivity determinations on corresponding concrete specimens (differing only in coarse aggregate type) were calculated. The mean difference and the standard deviation of the differences were calculated (see table 2). The standard deviation was calculated using the formula below:

$$s = \sqrt{\frac{\sum (\Delta_i - \bar{\Delta})^2}{n-1}}$$

where n ... sample size (number of differences)

Δ_i ... difference in chloride conductivity determinations on

corresponding concrete specimens differing only in coarse aggregate type

$\bar{\Delta}$ ... mean difference

From s and the mean conductivity, the coefficient of variation of the test determinations, cv_{det}, could be calculated. Note that the test results consisted of the mean of three test determinations. The coefficient of variation of the test results, cv_{res} would therefore be $1/\sqrt{3}$ the value of cv_{det} (see table 2).

Table 2: Effect of different coarse aggregates on the chloride conductivity results.

Durability index test	Mean conductivity	Mean difference (Greyw. - Gran.)	s	cv_{det} (cv_{res})	n
Chloride conductivity	2.38 mS/cm	-0.004 mS/cm	0.587 mS/cm	24.7 % (14.3 %)	12

The use of granite coarse aggregate instead of greywacke coarse aggregate did not cause any significant differences in the results of the chloride conductivity test. The mean difference was much smaller than the standard deviation of the individual differences. There was also no evidence to suggest that the differences changed with different curing regimes. This factor made it possible to combine the results of the greywacke and the granite 40 MPa mixes for each cement type for analysis purposes.

2.2 Aluminate content (C_3A)

One of the objectives of this project was to determine the effect of C_3A levels on the durability related properties of concrete. The experimental programme therefore included four Portland cement mixes with a range of C_3A levels (see table 3). However, these cements differed in terms of fineness and Alite/Belite ratio as well. This factor hampered the analysis as these factors often clouded the trends with C_3A.

The 40 MPa target strength mixes were used in the analysis. The results of the greywacke and granite mixes were combined.

The 40 MPa mixes differed in actual strengths (33 - 40 MPa) and w/c ratio (0.54 - 0.61) and could therefore not be compared in terms of C_3A content. The results were therefore adjusted to enable an equal strength C_3A comparison and an equal w/c ratio C_3A comparison.

For the equal strength comparison, the results of the mixes were adjusted to equivalent 40 MPa mixes (interpolating from the 20, 40 and 60 MPa target strength mixes). For the equal w/c ratio comparison, the results of the mixes were adjusted to equivalent 0.56 w/c ratio values (interpolating from the 20, 40 and 60 MPa target strength mixes).

The chloride conductivity values of the equivalent 40 MPa Portland cement mixes are displayed in table 3 and that of the equivalent 0.56 w/c ratio Portland cement mixes are displayed in table 4. The chloride conductivity results were normalised to exclude the effect of different curing regimes, by dividing the results for each curing period by the mean for that curing period for all cement types (see bottom halves of tables 3 and 4).

The equal strength comparison is shown graphically in figure 9 and the equal w/c ratio comparison in figure 10. In both cases the normalised chloride conductivity results are plotted against C_3A content.

The trends in figures 9 and 10 are ambiguous. The different slopes in figures 9 and 10 indicate that the results are governed by the basis of comparison (strength or w/c ratio). This is most likely a result of the other differences between the cements such as fineness and Alite/Belite ratio. It can therefore not be concluded from the results that C_3A content does or does not affect chloride conductivity. However it can be concluded that C_3A is unlikely to have a great effect on chloride conductivity.

This does not contradict other findings which state that C_3A improves chloride resistance, as the role of C_3A is chemical in nature (chloride binding), while the chloride conductivity test involves mainly the physical resistance of concrete to chloride ingress.

Table 3: Chloride conductivity results of equivalent 40 MPa Portland cement mixes.

Cement type	Chloride conductivities of equivalent 40 MPa Portland cement mixes (mS/cm)				C_3A content (%)
	Wet curing time (days)			Regression value (r = 0.71)	
	1d	7d	28d		
LASRC	2.74	2.53	2.25	2.48	0
Slurry SRC	2.94	2.04	2.05	2.32	1.9
De Hoek OPC	2.23	2.25	2.03	2.24	2.8
Riebeeck West OPC	2.30	2.05	1.98	2.07	4.8
Mean	2.55	2.22	2.08	2.28	
	Chloride conductivity / mean chloride conductivity				
LASRC	1.07	1.14	1.08	1.09	0
SRC	1.15	0.92	0.98	1.02	1.9
De Hoek	0.87	1.01	0.98	0.98	2.8
Riebeeck West OPC	0.90	0.92	0.95	0.91	4.8
Mean	1.00	1.00	1.00	1.00	

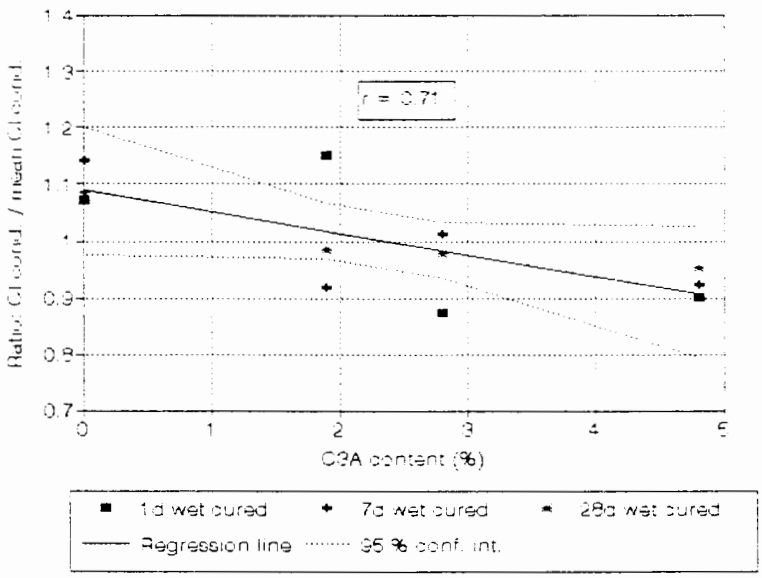

Figure 9: Ratio of chloride conductivity to mean chloride conductivity (for specific curing regime) of equivalent 40 MPa Portland cement mixes plotted against C_3A contents.

Table 4: Chloride conductivity results of equivalent 0.56 w/c ratio Portland cement mixes.

Cement type	Chloride conductivities of equivalent 0.56 w/c Portland cement mixes (mS/cm)				C_3A content (%)
	Wet curing time (days)			Regression value (r = 0.36)	
	1d	7d	28d		
LASRC	2.41	2.23	1.98	2.26	0
Slurry SRC	2.94	2.04	2.05	2.32	1.9
De Hoek	2.52	2.55	2.30	2.36	2.8
Riebeeck West OPC	2.57	2.29	2.21	2.43	4.8
Mean	2.61	2.28	2.13	2.34	
	Chloride conductivity / mean chloride conductivity				
LASRC	0.92	0.98	0.93	0.96	0
Slurry SRC	1.13	0.90	0.96	0.99	1.9
De Hoek	0.97	1.12	1.08	1.01	2.8
Riebeeck West OPC	0.99	1.01	1.04	1.04	4.8
Mean	1.00	1.00	1.00	1.00	

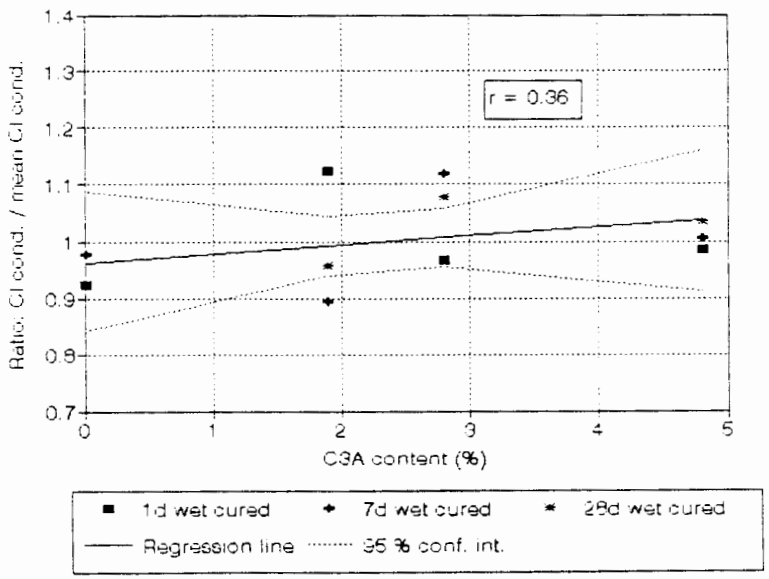

Figure 10: Ratio of chloride conductivity to mean chloride conductivity (for specific curing regime) of the equivalent 0.56 w/c ratio mixes versus C_3A contents.

2.3 Alite/Belite ratio

Another objective of this project was to determine the effect of Alite/Belite ratio on the durability related properties of concrete. Only the LASRC cement had a markedly different Alite/Belite ratio from the other Portland cements (see chapter 4). The selection of cements was therefore not ideally suited for such an analysis.

From figures 9 and 10 there is no conclusive evidence to suggest that the LASRC mix (C_3A = 0 %; Alite/Belite ratio = 4.2) performed any better or any worse compared with the other 3 Portland cement mixes (Alite/Belite ratios: 2.1 - 2.7).

2.4 OPC vs blended cements

Chloride isoconductivity graphs were drawn to compare the OPC mixes with the blended cement mixes. The blended cement mixes included 30 % and 50 % fly ash mixes and 50 % and 70 % slag mixes. Riebeeck West OPC was used for most of the blends (20, 40 and 60 MPa target strengths), but the 40 MPa blended mixes were repeated with De Hoek OPC as well. The results of the pairs of 40 MPa mixes (De Hoek and Riebeeck West) were averaged for the isoconductivity graphs. This could be done since the variation of the results was larger than the differences (due to different C_3A contents). The purpose of this was to represent the performance of a general Western Cape OPC blended mix, and to reduce the variation in results caused by small sample sizes.

An isoconductivity graph is drawn by plotting the nine conductivity values of the mixes containing one cement type (3 target strengths x 3 curing regimes) on a graph with w/c ratio on the Y-axis and curing on the X-axis, and then interpolating isoconductivity lines between these points (see Appendix 2). By interpolating the data, individual results that might have appeared inconsistent or anomalous would be masked as the isoconductivity lines are influenced by the general trend of results. Figure 11 shows chloride isoconductivity plots for the OPC, 30 % fly ash and 50 % slag mixes and figure 12 shows chloride isoconductivity plots for the 50 % fly ash and the 70 % slag mixes The individual results of each mix are plotted in figures 13, 14 and 15 to show the consistency of the trends. Note that the strength labels given on these figures reflect the target strengths and not the actual strengths.

The horizontal spacing between a series of isoconductivity lines gives an indication of the sensitivity to curing, while vertical spacing gives an indication of the sensitivity to w/c ratio. A series of horizontally-tending isoconductivity lines would indicate a sensitivity to w/c ratio, but not to curing, while vertically tending lines would indicate a sensitivity to curing.

The isoconductivity graphs are useful for choosing the correct w/c ratio and curing regime to achieve a specific chloride conductivity.

From figure 11:

1) The OPC mixes were not very sensitive to curing in contrast with the fly ash and slag mixes.
2) All the mixes were less sensitive to curing at higher strengths (low w/c), and more sensitive to curing at lower strengths (high w/c).
3) A decrease in w/c ratio significantly decreased the chloride conductivity of all the OPC mixes and of the fly ash and slag mixes moist cured for shorter periods. The fly ash and slag mixes cured for longer periods had very low chloride conductivities and were less sensitive to w/c ratio than the OPC mixes.
4) Substantially lower chloride conductivities were obtained using fly ash or slag mixes with w/c ratios of 0.5 and lower, regardless of curing, and also for well cured concretes (7 days moist curing and more) regardless of w/c ratio. Only the inadequately cured fly ash and slag mixes with high w/c ratios (1 day moist cured, w/c = 0.8) did not show an improvement over OPC.
5) The slag mixes wet cured for 1 - 7 days performed slightly better compared with the corresponding fly ash mixes. The slag mixes continued to improve with additional wet curing (after 7 days), which resulted in significantly lower chloride conductivities after 28 days wet curing compared with the fly ash mixes.

Figure 12 shows chloride isoconductivity plots for the 50 % fly ash and the 70 % slag mixes.

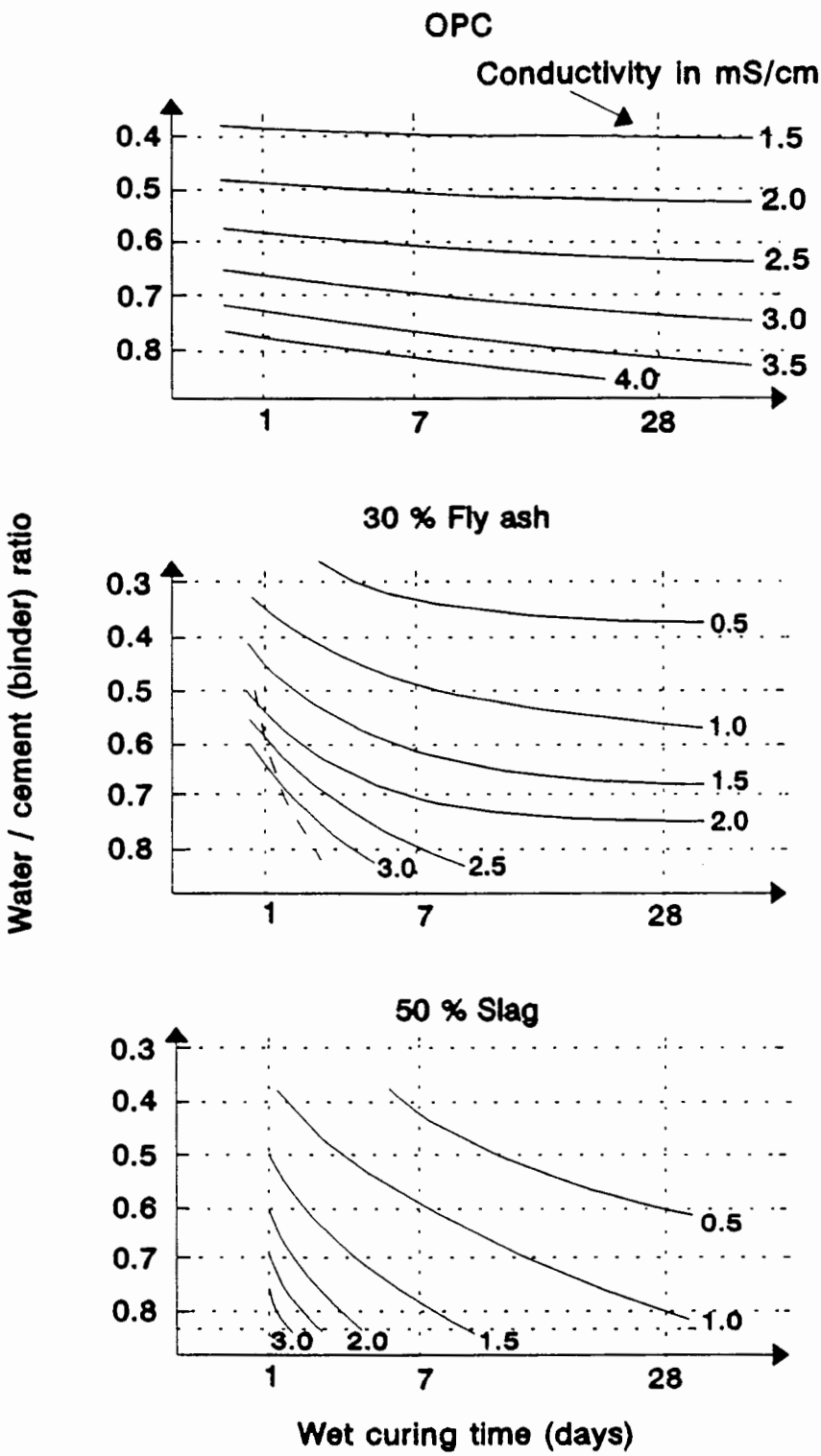

Figure 11:Chloride isoconductivity graphs: OPC, 30 % fly ash, 50 % slag mixes.

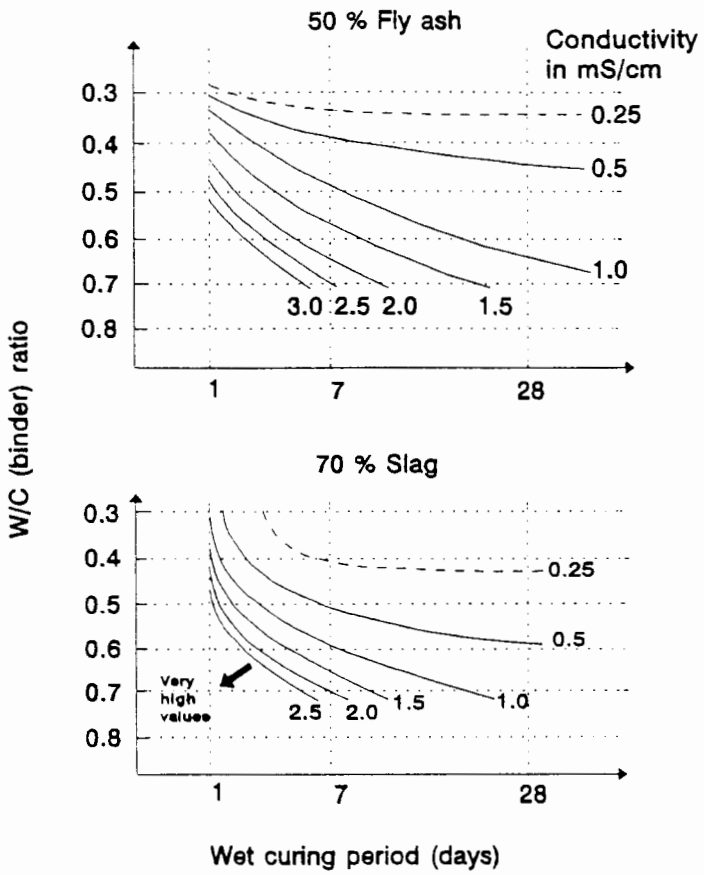

Figure 12:Chloride isoconductivity graphs: 50 % fly ash and 70 % slag mixes.

Generally the trends found in figure 11 were magnified by the higher replacement levels.

1) The high replacement fly ash and slag mixes with high w/c ratios (> 0.6) became more sensitive to curing compared with the low replacement fly ash and slag mixes. However, for low w/c ratios (< 0.4), the high replacement mixes were similar with regard to curing sensitivity as the low replacement mixes.

2) The high replacement mixes with low w/c ratios (< 0.4) had substantially lower (50 - 70 % less) chloride conductivities compared with the low replacement mixes.

3) In contrast, the high replacement mixes with high w/c ratios (> 0.6) and wet cured for only 1 day had higher chloride conductivity values compared with the low replacement mixes.

4) Generally the 70 % slag mixes had slightly lower conductivities compared with the 50 % fly ash mixes if wet cured for 7 or more days. The opposite was true for the 1 day wet cured mixes where the 50 % fly ash mixes had the lower conductivities.

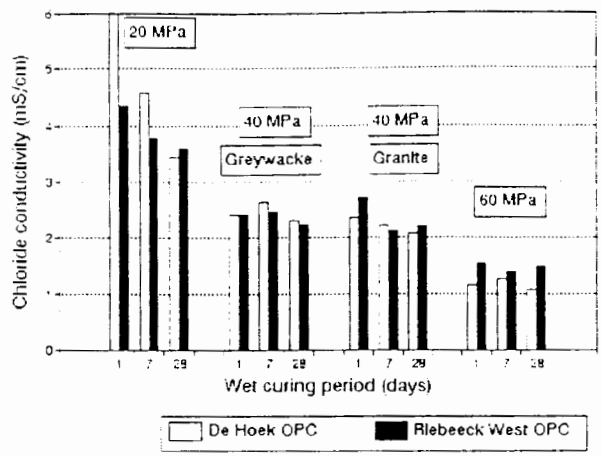

Figure 13: Chloride conductivity results of the OPC mixes.

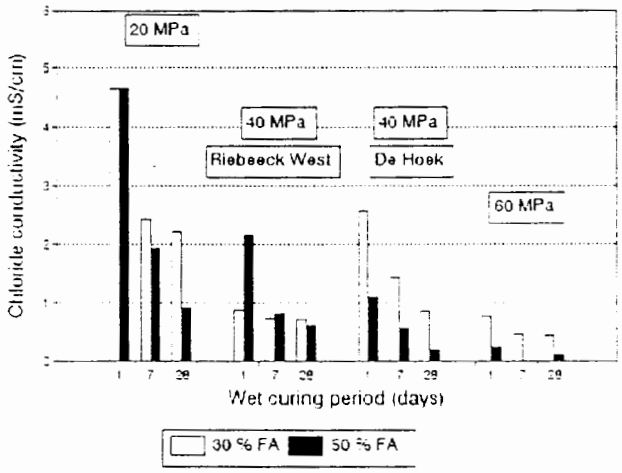

Figure 14: Chloride conductivity results of the fly ash mixes.

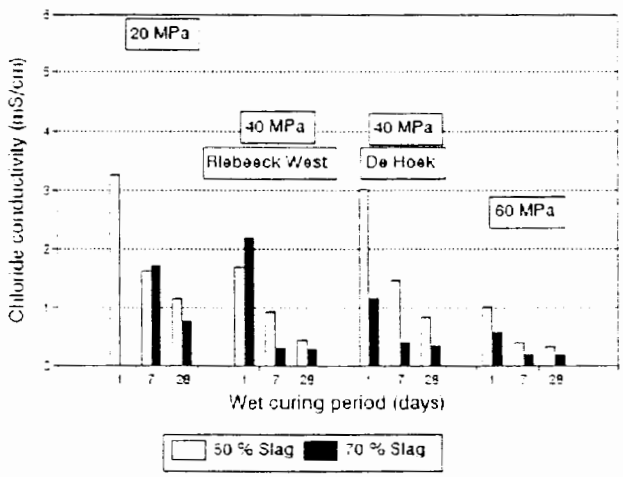

Figure 15: Chloride conductivity results of the slag mixes.

2.5 Reduction in chloride conductivity (2 week chloride conductivity test)

The reduction in chloride conductivity was represented as the percentage difference between the two chloride test results relative to the initial chloride conductivity test result (see equation 2).

$$Reduc.\ \% = \frac{Cl^- \ cond. - 2 \ week \ Cl^- \ cond.}{Cl^- \ conductivity} \times 100\ \% \qquad \textbf{(A1.2)}$$

The results of all the Portland cement mixes are displayed in table 5. The reduction percentages calculated from the 1, 7 and 28 day wet cured samples were averaged ie. only one value per mix is displayed in table 5.

Table 5: Reductions in chloride conductivity after 2 weeks immersion in chloride solution (Portland cements).

Cement	Mix no.	Cube strength (MPa)	w/c	Reduction %
Slurry SRC C_3A = 1.8 %	1	20	0.85	6 %
	2	40	0.56	35 %
De Hoek OPC C_3A = 2.8 %	4	15	0.83	33 %
	5	35	0.54	47 %
	6	40	0.54	35 %
	7	60	0.36	45 %
LASRC C_3A = 0 %	8	20	0.87	22 %
	9	40	0.61	31 %
	10	40	0.61	35 %
	11	50	0.42	14 %
Riebeeck West OPC C_3A = 4.8 %	12	20	0.83	31 %
	13	33	0.56	46 %
	14	35	0.56	47 %
	15	60	0.33	65 %

C_3A levels are reported to be an important factor responsible for chloride binding in Portland cement mixes. The values in table 5 cannot be compared on a C_3A basis since the cube strengths and w/c ratios of the mixes differ. The reduction values were therefore plotted versus w/c ratio (figure 16) and cube strength (figure 17) to determine a general relationship between reduction percentages, w/c ratio and cube strength.

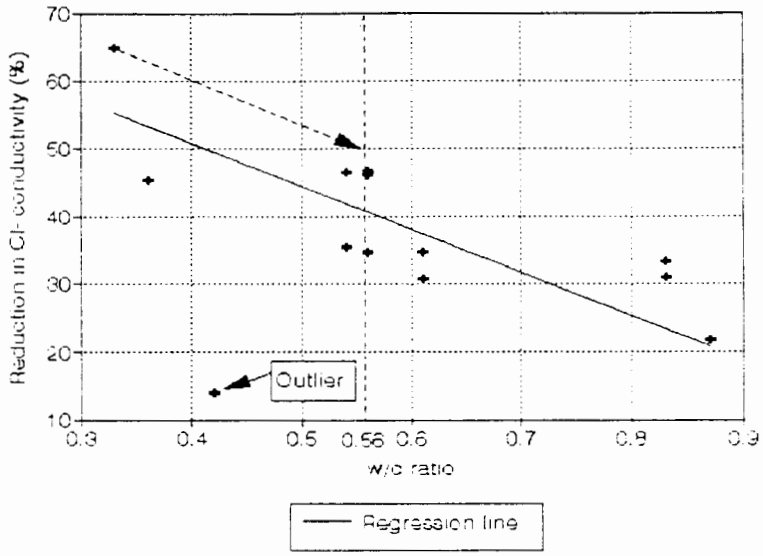

Figure 16: Reduction in conductivity plotted against w/c ratio (Portland cement mixes).

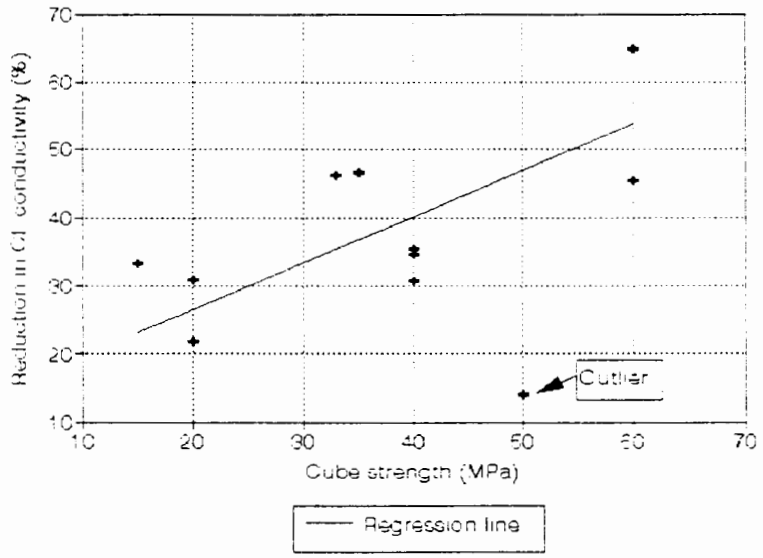

Figure 17: Reduction in chloride conductivity plotted against cube strength (Portland cement mixes).

The reduction percentages were then adjusted to that of an equivalent 0.56 w/c ratio PC mix

and that of an equivalent 40 MPa PC mix. This was done by moving the data points parallel to the regression line to the 0.56 w/c (figure 16) and 40 MPa (figure 17) levels. The adjusted values displayed in table 6 can then be compared on a C_3A basis.

Table 6: Reductions in chloride conductivity after 2 weeks immersion in chloride solution (Portland cements) adjusted to equivalent 0.56 w/c ratio and 40 MPa mixes.

C_3A %	Reduction of equivalent 0.56 w/c mix	Reduction of equivalent 40 MPa mix
0	5 %	7 %
0	34 %	31 %
0	38 %	35 %
0	42 %	35 %
1.8	27 %	22 %
1.8	35 %	35 %
2.8	33 %	32 %
2.8	34 %	35 %
2.8	45 %	50 %
2.8	50 %	50 %
4.8	46 %	45 %
4.8	47 %	50 %
4.8	48 %	51 %
4.8	50 %	51 %

Figure 18 and 19 shows the adjusted reduction values plotted against C_3A content. Figure 18 was done on an equal w/c ratio (0.56) basis and figure 19 was done on an equal cube strength (40 MPa) basis.

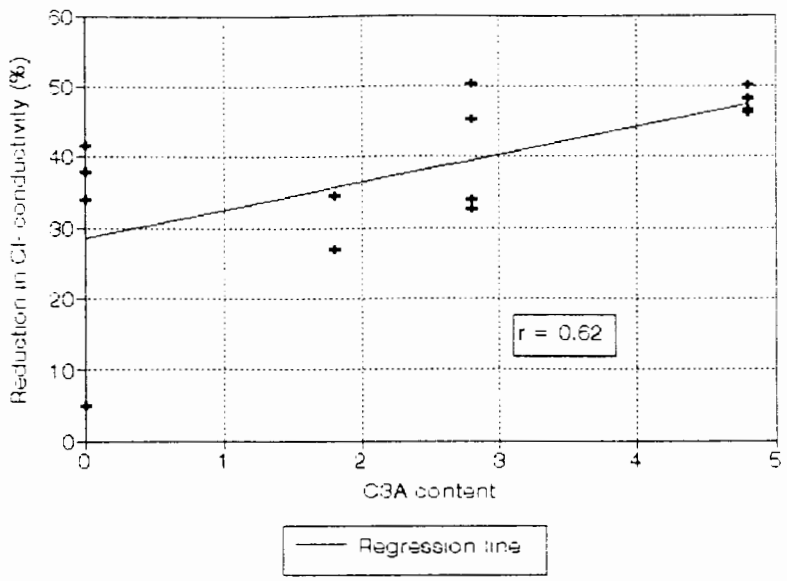

Figure 18: Reduction in chloride conductivity plotted against C_3A level (for equivalent 0.56 w/c ratio PC mixes).

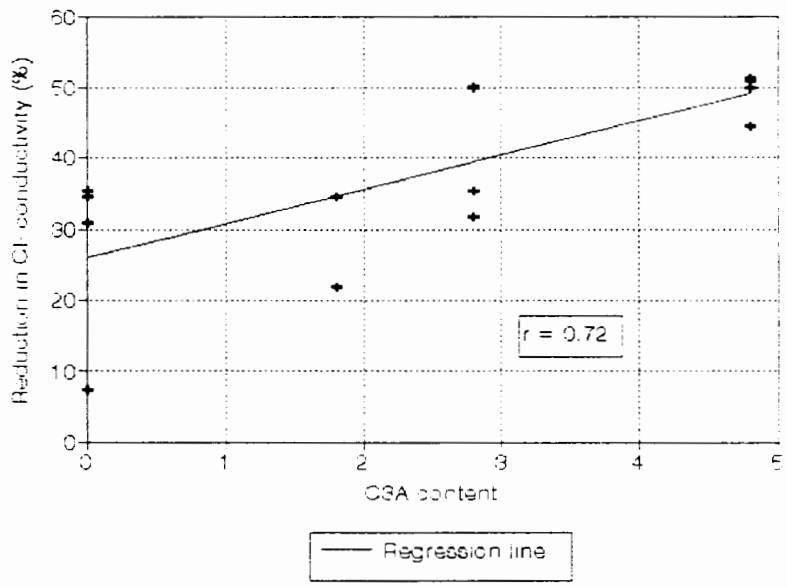

Figure 19: Reduction in chloride conductivity plotted against C_3A levels (values adjusted for equivalent 40 MPa PC mixes).

The correlation coefficients of r = 0.62 and 0.72 indicate a statistically significant correlation between C_3A levels and reduction percentages (The 95 % critical r value for a sample size of 12 is 0.54 (Chatfield, 1970, p. 190)). The lower correlation coefficient in figure 18 is probably a result of other differences between the Portland cements.

The increase in reduction percentage of 4.7 % with every 1 % increase in C_3A content is substantial relative to the range of results generally found (see table 7).

The results of the blended cements are displayed in table 7. Reductions in chloride conductivity over the two weeks were least for the OPC mixes (44 % mean), somewhat more for the fly ash mixes (54 % mean) and greatest for the slag mixes (70 % mean). Note that the 40 MPa results included 2 mixes and were weighted double that of the other results when the mean values were calculated.

Table 7: Reductions in conductivity after 2 weeks immersion in chloride solution (blended cements).

Cement type	Wet curing period (days)	Percentage reduction in chloride conductivity (%)			
		Target strength (MPa)			Mean
		20	40	60	
OPC	1	36	45	58	46
	7	28	46	54	44
	28	36	40	54	43
	Mean	33	44	55	44
OPC/fly ash 70/30	1	58	48	64	54
	7	54	47	59	52
	28	57	57	52	56
	Mean	56	51	58	54
OPC/slag 50/50	1	53	84	86	77
	7	52	78	70	70
	28	55	66	66	63
	Mean	53	76	74	70

Trends of chloride conductivity with strength depended on cement type. Generally, greater reductions occurred for the higher strength mixes. There was also a general trend of greater reductions in conductivity for mixes cured for shorter periods. This is probably due to additional hydration during the 2 weeks.

Extrapolating from figure 19 indicates that a Portland cement would need a C_3A content of approximately 10 % to equal the reduction factors of slag cements. Note however that this level (10 %) is far above the range of C_3A levels tested (0 % - 4.8 %).

The reduction in conductivity was mainly ascribed to a change in the physical pore structure (increase in tortuosity and constrictivity of the pores) due to the presence of chloride ions, and to a lesser degree to:

1. Reduction in pore solution conductivity. Previous work has shown that a 35 % reduction in chloride concentration (from 5 M NaCl) results in only about a 14 % reduction in conductivity (Streicher and Alexander, 1995).
2. Additional hydration. The differences between samples cured for shorter periods before re-saturation for the conductivity test, and those cured for a full 28 days, are relatively small, except possibly for the slag mixes. In contrast, the OPC mixes which were insensitive to initial curing (figure 12) showed a substantial reduction in conductivity. This would seem to indicate that additional hydration from delayed curing has a minor influence.

Verification for the above hypothesis also comes from results of another series of tests using a modified version of the Dundee rapid chloride test (Dhir et al, 1990), where the electric potential was maintained for a period of 14 days (Streicher et al, 1994). A continuous flux of chloride ions flowed through the specimen preventing the depletion of chloride ions due to binding. A reduction in chloride flux occurred with time, as measured by electric current.

Mackechnie (1996) performed chloride conductivity tests in our laboratory on a range of specimens immersed in 5 M NaCl solutions (after 28 days moist curing) for various periods up to 98 days. A rapid reduction occurs in the first two weeks (28 - 42 days) followed by a more gradual reduction up to 98 days. Mackechnie stated that correlations between chloride conductivity values and two-year apparent diffusion coefficients of marine exposed concretes were improved substantially when 98 day chloride conductivity values were used instead of 28 day values. The improved correlations were probably due to both the effect of the presence of chlorides on the diffusibility of the material, and additional curing (since the on-site exposed concretes also underwent additional curing).

3. Summary

3.1 The use of two different coarse aggregates, ie. greywacke and granite, did not cause significant differences in the chloride conductivity test results.

3.2 Aluminate content (C_3A): An increase in aluminate content resulted in a decrease in chloride conductivity results when Portland cement concretes were compared on the basis of equal strengths (40 MPa). However, when Portland cement concretes were compared on the basis of equal w/c ratio, there was no significant correlation. This discrepancy is explained by the wide range of differences between the Portland cements (eg. fineness, Alite/Belite ratio). It was concluded that C_3A does not cause a significant decrease in chloride conductivity results, over the relatively narrow range of C_3A values considered, i.e. 0 % - 4.8 %. A lower chloride conductivity mainly indicates an improved physical resistance of concrete to chloride ingress.

An increase in aluminate content increased the reduction in conductivity after 2 weeks immersion in the chloride solution substantially. A 1 % increase in C_3A increased the reduction by 4.9 %. A higher reduction factor indicates an improved chemical resistance of concrete to chloride ingress.

3.3 Alite/Belite ratio: There was no evidence to suggest that Alite/Belite ratio had a significant effect on the chloride conductivity test results.

3.4 Blended mixes: Isoconductivity graphs were drawn for the OPC mixes and the blended cement mixes. The isolines connect points with equal conductivity values on graphs with w/c ratio on the Y-axis and wet curing period on the X-axis.

The isoconductivity graphs showed that the OPC mixes were not as sensitive to curing as the blended cement mixes, in terms of chloride conductivity.

The isographs showed that all the mixes became less sensitive to curing at lower w/c ratios. The mixes also became less sensitive to curing with time, although the slag mixes showed this to a lesser degree (ie. there was still a significant improvement

with curing after 7 days).

In general, substantially better durability index levels were obtained with blended cement mixes provided the mixes had low w/c ratios (0.3 - 0.4), **or** the mixes were cured well (7 - 28 days wet curing). The performance of blended cement mixes of w/c > 0.4 and with only 1 day wet curing was in general similar or slightly worse compared with corresponding OPC mixes.

The 50 % slag mixes generally performed better compared with the 30 % fly ash mixes in terms of chloride conductivity (between 10 % and 50 % lower conductivities).

3.5 High replacement blended mixes: The use of higher replacement levels (50 % fly ash and 70 % slag) increased the sensitivity of the blended mixes to curing. Both mixes had substantially lower chloride conductivity values compared with the low replacement mixes (30 % fly ash and 50 % slag), provided they had low w/c ratios (< 0.5) or they were cured well (> 7 days).

3.6 Blended cements (chloride binding): Chloride conductivity tests were repeated on all the concrete samples after soaking for two weeks in a 5 M NaCl solution (2 week chloride conductivity test). A reduction was observed in chloride conductivity in the 2 week test thought to be due to a combination of a change in the pore structure and a reduction in the pore solution conductivity from chloride binding. The reduction factors calculated for OPC varied between 33 and 57 %, for 30 % fly ash between 50 % and 60 %, and for 50 % slag between 55 % to 76 %. The use of fly ash increased the reduction slightly (compared with OPC), while the use of slag increased the reduction significantly. This reduction generally increased with strength possibly because of the higher cement content.

4. Conclusions and recommendations

The physical resistance of Portland cement concrete to chloride ingress is not improved significantly by higher C_3A contents, while the chemical resistance to chloride ingress is

improved appreciably by higher C_3A contents, within the range of C_3A levels from 0 % to 4.8 %. The physical resistance was assessed by means of the initial chloride conductivity test, while the chemical binding effects were assessed by means of the reduction in conductivity after two weeks immersion in the chloride solution. Different Alite/Belite ratios did not cause any statistically significant changes to any of the durability properties tested.

By blending cements with fly ash or slag, both the physical and the chemical resistance to chloride ingress are improved substantially compared with that of the Portland cement mixes. The blended mixes are however more sensitive to curing and would require strict specifications in terms of curing.

5. References

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Streicher, P.E. and Alexander, M.G., A chloride conduction test for concrete, *Cement and Concrete Research*, Vol. 25, No. 6, 1995, pp. 1284-1294.

Table 1: Compressive cube strength results.
('*' 5 - 15 % under strength, '**' 15 - 25 % under strength, '***' > 25 % under strength).

Mix number	Compressive strengths of cubes after 3, 7, 28 and 90 days wet curing (MPa) (Mean of three cubes)				Target strength (MPa)
	3 days	7 days	28 days	90 days	28 days
1	11.8	15.5	20.0	20.4	20
2	25.0	30.1	39.8	45.1	40
3	27.2	33.-	39.8	44.9	40
4	10.0	11.7	15.1**	19.0	20
5	22.7	27.6	34.8*	41.1	40
6	23.1	29.1	39.2	43.7	40
7	44.0	52.6	60.7	68.1	60
8	11.5	15.2	20.2	26.4	20
9	24.2	30.1	38.1	46.3	40
10	21.5	28.7	39.3	45.1	40
11	36.8	45.4	50.6**	57.4	60
12	10.3	16.3	19.1	23.9	20
13	19.0	27.1	33.0**	40.2	40
14	20.5	29.5	35.3*	41.0	40
15	38.3	53.0	60.0	71.7	60
16	8.6	12.9	19.8	29.3	20
17	19.3	27.6	39.5	52.0	40
18	33.8	45.1	59.9	76.8	60
19	8.0	12.9	21.9	30.4	20
20	18.1	26.5	41.8	57.5	40
21	28.8	42.0	63.1	79.2	60
22	11.4	13.9	20.4	24.7	20
23	18.1	27.5	41.8	53.1	40
24	16.7	24.5	39.8	55.4	40
25	5.1	10.1	20.9	25.3	20

Table 1 - continued

Mix number	Compressive strengths of cubes after 3, 7, 28 and 90 days wet curing (MPa) (Mean of three cubes)				Target strength (MPa)
	3 days	7 days	28 days	90 days	28 days
26	10.3	16.6	34.1*	45.1	40
27	22.5	36.6	59.5	76.2	60
28	6.6	13.8	31.9**	41.2	40
29	9.4	22.2	36.2*	43.6	40
30	10.6	14.3	19.7	24.5	20
31	14.2	18.1	26.5***	not tested	40
32	19.6	27.0	35.8*	49.8	40
33	21.2	28.3	35.2***	not tested	60
34	4.4	8.3	19.6	not tested	20
35	11.2	17.5	36.1*	42.5	40
36	21.6	35.4	54.9*	63.9	60

Table 2: Summary of results (mean values).

('*' Maximum acceptable range of individual test determinations exceeded.)

Cement type	Mix no.	Target strength (MPa)	Wet curing period (days)	Water sorptivity (mm/√h)	Oxygen permeability index	Chloride conductivity (mS/cm)
Slurry SRC	1	20	1	20.0	8.50	2.80
			7	22.4	8.74	2.71
			28	19.1	8.83	2.43
	2	40	1	21.5	9.10	2.61
			7	18.1	9.41	2.05
			28	13.8	9.74	1.92
	3	40	1	21.6	9.05	3.26
			7	15.7	9.78	2.03
			28	16.5	9.80	2.17
De Hoek OPC	4	20 (Actual = 15)	1	24.1	8.22	7.69*
			7	24.3	8.27	4.59
			28	16.2	9.01	3.44
	5	40 (35)	1	15.9	8.93	2.42
			7	12.0	9.33	2.62
			28	11.6	9.32	2.30
	6	40	1	30.2	8.65	2.35
			7	30.8	9.13	2.21
			28	16.9	9.55	2.06
	7	60	1	10.1	9.38	1.15
			7	11.6	9.28	1.26
			28	9.2	9.83	1.07
LASRC	8	20	1	31.0	8.45	4.36
			7	22.5	8.93*	3.64
			28	17.2	8.99*	4.15
	9	40	1	26.9	not tested	2.95
			7	20.3	not tested	2.38
			28	17.1	not tested	2.21
	10	40	1	18.3*	8.49	2.52
			7	15.8*	9.57	2.68
			28	14.0	9.89	2.29
	11	60 (51)	1	13.7	7.84	1.76
			7	16.5	8.28	1.51
			28	13.8	9.31	1.31
Riebeeck West OPC	12	20	1	20.3	8.28	4.34
			7	15.6	9.05	3.77
			28	13.4	9.34	3.59

Table 2 - continued

Cement type	Mix no.	Target strength (MPa)	Wet curing period (days)	Water sorptivity (mm/√h)	Oxygen permeability index	Chloride conductivity (mS/cm)
	13	40 (33)	1	16.7	9.22	2.42
			7	15.2	9.39	2.46
			28	12.5	9.83	2.22
	14	40 (35)	1	18.5	8.61*	2.71
			7	11.0	9.89	2.12
			28	12.3	9.88	2.20
	15	60	1	8.2	8.88	1.54
			7	7.7	9.03	1.39
			28	7.9*	9.96	1.48
30 % fly ash / 70 % Riebeeck West OPC	16	20	1	21.3	8.24	4.66
			7	16.0	9.18	2.42
			28	11.6*	9.49	2.21
	17	40	1	14.0	9.28	0.88
			7	8.7	9.98	0.73
			28	8.2	9.81	0.70
	18	60	1	5.9	8.83*	0.76*
			7	5.4*	9.49	0.46
			28	5.9	9.39	0.44*
50 % fly ash / 50 % Riebeeck West OPC	19	20	1	18.5	8.31	4.65
			7	10.0	9.63	1.92
			28	5.0	10.14	0.91
	20	40	1	16.2	9.07	2.16*
			7	8.1	10.19	0.80
			28	5.2	10.51	0.61
	21	60	1	4.8*	9.61	0.22
			28	3.3	10.67*	0.11
De Hoek OPC (repeat)	22	20	1	12.1	8.78	2.88
			7	13.2	8.93	2.76
			28	7.5	9.33*	2.18
30 % fly ash/ 70 % De Hoek OPC	23	40	1	15.7	9.08	2.56
			7	10.4	9.76	1.43
			28	8.2	10.35	0.85
50 % fly ash/ 50 % De Hoek OPC	24	40	1	16.3	9.07	1.09
			7	11.2	9.39	0.54
			28	5.9	10.13*	0.20
50 % slag / 50 % Riebeeck West OPC	25	20	1	18.1	8.40	3.27
			7	11.2	8.87	1.61

Table 2 - continued

Cement type	Mix no.	Target strength (MPa)	Wet curing period (days)	Water sorptivity (mm/√h)	Oxygen permeability index	Chloride conductivity (mS/cm)
			28	6.8	9.09	1.15
	26	40 (34)	1	18.4	8.65	1.68
			7	7.8	9.60	0.92*
			28	5.7	9.29	0.44
	27	60	1	14.8*	9.18	1.02
			7	6.3	9.95	0.40
			28	5.3*	10.02	0.32
50 % slag / 50 % De Hoek OPC	28	40 (32)	1	18.7	8.23	3.01
			7	10.7	9.12	1.46
			28	7.0	9.70	0.82
70 % slag / 30 % De Hoek OPC	29	40 (36)	1	9.6	8.87	1.15*
			7	4.7	9.63	0.39
			28	3.8	9.92	0.34
White cement	30	20	1	18.4	8.07	2.06
			7	16.5	8.74	1.31
			28	11.7	9.22	1.40
	32	40 (36)	1	17.9	8.52	2.73
			7	13.0	9.35	2.12
			28	10.0	9.83	2.18
70 % slag / 30 % Riebeeck West OPC	34	20	1	The concrete cubes were too weak for the coring procedure		
			7		8.61	1.7
			28		9.26	0.76
	35	40 (36)	1	21.1	8.51	2.19
			7	9.6	9.31	0.30*
			28	6.1	9.88	0.28
	36	60 (55)	1	7.9*	9.06	0.57
			7	4.4	9.92	0.18
			28	3.7	9.50	0.17

Table 3: Chloride conductivity results.
(* Maximum acceptable range of individual test determinations exceeded.)

Mix number	Wet curing time (days)	Initial conductivity (μS/cm)	Chloride conductivity (mS/cm)	2 week chloride conductivity (mS/cm)
1	1	310	2.97	4.39
		253	2.55	3.30
		324	2.88	2.28
	Average	295	2.80	3.32
	Coefficient of variation	12.6%	7.9%	31.8%
	7	249	2.97	3.22
		229	2.64	2.83
		238	2.53	1.79
	Average	239	2.71	2.62
	Coefficient of variation	4.1%	8.4%	28.2%
	28	229	2.45	1.89
		190	2.34	2.51
		250	2.50	1.89
	Average	223	2.43	2.10
	Coefficient of variation	13.6%	3.3%	16.8%
2	1	260	2.78	2.21
		226	3.12	1.23
		131	1.94*	1.18
	Average	205	2.61	1.54
	Coefficient of variation	32.6%	23.1%	38.0%
	7	190	1.97	1.84
		168	2.05	1.06
		137	2.13	1.59
	Average	165	2.05	1.50
	Coefficient of variation	16.1%	3.8%	26.5%
	28	174	2.04	1.14
		140	1.73	1.43
		146	1.98	1.13
	Average	153	1.92	1.23
	Coefficient of variation	11.8%	8.5%	13.8%
3	1	248	3.03	0.78 - 4 week
		350	3.88	0.93 - " "
		248	2.88	0.79 - " "
	Average	282	3.26	0.83 - " "

Table 3 - continued

Mix number	Wet curing time (days)	Initial conductivity (μS/cm)	Chloride conductivity (mS/cm)	2 week chloride conductivity (mS/cm)
	Coefficient of variation	20.9%	16.6%	10.3%
	7	279	2.01	0.76 - 4 week
		191	1.84	0.70 - " "
		248	2.23	0.79 - " "
	Average	239	2.03	0.75 - " "
	Coefficient of variation	18.6%	9.5%	6.1%
	28	218	2.09	0.82 - 4 week
		224	2.05	0.81 - " "
		252	2.35	0.90 - " "
	Average	232	2.17	0.84 - " "
	Coefficient of variation	7.9%	7.6%	5.5%
4	1	534	10.49	3.87
		657	7.05	5.42
		402	5.52	4.14
	Average	531	7.69*	4.48
	Coefficient of variation	24.1%	33.1%	18.4%
	7	305	4.46	3.30
		308	4.57	3.27
		377	4.72	3.43
	Average	330	4.59	3.33
	Coefficient of variation	12.3%	2.8%	2.6%
	28	295	3.24	1.79
		266	4.01	2.66
		301	3.07	1.85
	Average	288	3.44	2.10
	Coefficient of variation	6.4%	14.6%	23.2%
5	1	264	2.38	1.41
		438	2.81	1.25
		325	2.06	1.32
	Average	343	2.42	1.33
	Coefficient of variation	25.7%	15.5%	6.1%
	7	255	2.56	1.12
		279	2.41	1.56
		222	2.90	1.08

Table 3 - continued

Mix number	Wet curing time (days)	Initial conductivity (μS/cm)	Chloride conductivity (mS/cm)	2 week chloride conductivity (mS/cm)
	Average	252	2.62	1.25
	Coefficient of variation	11.3%	9.5%	21.6%
	28	240	2.01	1.42
		284	2.92*	1.29
		246	1.99	1.26
	Average	257	2.30	1.33
	Coefficient of variation	9.4%	23.0%	6.4%
6	1	255	2.12	1.55
		457	2.68	2.00
		404	2.25	1.45
	Average	372	2.35	1.67
	Coefficient of variation	28.2%	12.6%	17.4%
	7	264	2.37	1.51
		278	2.01	1.21
		238	2.25	1.26
	Average	260	2.21	1.33
	Coefficient of variation	7.7%	8.3%	11.9%
	28	278	1.93	1.32
		289	2.29	1.39
		301	1.97	1.17
	Average	289	2.06	1.29
	Coefficient of variation	4.0%	9.5%	8.6%
7	1	146	1.06	0.53
		149	1.06	0.55
		155	1.31	0.70
	Average	150	1.15	0.59
	Coefficient of variation	2.9%	12.2%	16.0%
	7	150	1.15	0.68
		189	1.41	0.68
		172	1.23	0.69
	Average	170	1.26	0.68
	Coefficient of variation	11.6%	10.5%	1.3%
	28	136	1.14	0.65
		143	0.93	0.56

Table 3 - continued

Mix number	Wet curing time (days)	Initial conductivity (μS/cm)	Chloride conductivity (mS/cm)	2 week chloride conductivity (mS/cm)
		139	1.14	0.68
	Average	139	1.07	0.63
	Coefficient of variation	2.7%	11.1%	9.6%
8	1	299	5.03	4.31
		268	3.34*	2.28
		348	4.70	3.91
	Average	305	4.36	3.50
	Coefficient of variation	13.4%	20.5%	30.7%
	7	252	3.88	2.90
		280	3.86	2.96
		286	3.18	2.05
	Average	273	3.64	2.64
	Coefficient of variation	6.5%	10.9%	19.2%
	28	273	4.96	4.48
		269	3.97	3.08
		222	3.51	2.65
	Average	255	4.15	3.40
	Coefficient of variation	11.0%	17.9%	28.1%
9	1	285	3.25	2.23
		284	3.08	2.19
		196	2.50	1.62
	Average	255	2.95	2.01
	Coefficient of variation	19.9%	13.3%	17.0%
	7	211	2.52	1.72
		206	2.38	1.55
		200	2.24	1.57
	Average	205	2.38	1.61
	Coefficient of variation	2.7%	5.9%	5.6%
	28	201	2.30	1.64
		218	2.18	1.58
		217	2.15	1.55
	Average	212	2.21	1.59
	Coefficient of variation	4.5%	3.6%	2.8%
10	1	322	2.61	1.79

Table 3 - continued

Mix number	Wet curing time (days)	Initial conductivity (μS/cm)	Chloride conductivity (mS/cm)	2 week chloride conductivity (mS/cm)
		322	2.54	1.56
		262	2.40	1.40
	Average	302	2.52	1.58
	Coefficient of variation	11.6%	4.2%	12.4%
	7	216	3.43**	2.21
		242	2.28	1.15
		228	2.33	1.81
	Average	229	2.68	1.72
	Coefficient of variation	5.5%	24.1%	31.0%
	28	357	1.97	1.26
		193	2.17	1.39
		347	2.75*	2.08
	Average	299	2.29	1.58
	Coefficient of variation	30.6%	17.7%	27.9%
11	1	284	1.77	1.64
		358	1.90	1.66
		234	1.61	1.40
	Average	292	1.76	1.57
	Coefficient of variation	21.4%	8.3%	9.2%
	7	250	1.58	1.38
		208	1.44	1.47
		218	1.52	0.95
	Average	226	1.51	1.27
	Coefficient of variation	9.7%	4.6%	21.8%
	28	217	1.44	1.22
		152	1.26	1.07
		171	1.24	1.03
	Average	180	1.31	1.11
	Coefficient of variation	18.5%	8.3%	9.3%
12	1		4.35	2.76
			4.06	3.12
			4.62	3.23
	Average		4.34	3.04
	Coefficient of variation		6.4%	8.1%

Table 3 - continued

Mix number	Wet curing time (days)	Initial conductivity (μS/cm)	Chloride conductivity (mS/cm)	2 week chloride conductivity (mS/cm)
	7		3.61	2.57
			3.85	2.60
			3.86	2.87
	Average		3.77	2.68
	Coefficient of variation		3.7%	6.1%
	28		3.45	2.31
			3.65	2.34
			3.69	2.47
	Average		3.59	2.37
	Coefficient of variation		3.5%	3.6%
13	1	161	2.45	1.15
		168	2.48	1.11
		155	2.31	1.18
	Average	161	2.42	1.15
	Coefficient of variation	4.3%	3.8%	2.9%
	7	175	2.35	1.37
		157	2.45	1.29
		159	2.57	1.29
	Average	164	2.46	1.32
	Coefficient of variation	6.0%	4.5%	3.1%
	28	179	2.39	1.37
		186	2.26	1.39
		178	2.00	1.26
	Average	181	2.22	1.34
	Coefficient of variation	2.3%	8.9%	5.2%
14	1	210	2.71	1.33
		224	2.66	1.16
		189	2.77	1.35
	Average	208	2.71	1.28
	Coefficient of variation	8.5%	2.1%	8.0%
	7	174	2.16	1.12
		197	2.05	1.13
		169	2.15	1.19
	Average	180	2.12	1.14

Table 3 - continued

Mix number	Wet curing time (days)	Initial conductivity (μS/cm)	Chloride conductivity (mS/cm)	2 week chloride conductivity (mS/cm)
	Coefficient of variation	8.5%	2.8%	3.3%
	28	229	2.43	1.39
		186	2.22	1.33
		191	1.95	1.18
	Average	202	2.20	1.30
	Coefficient of variation	11.8%	10.9%	8.4%
15	1	152	1.56	0.48
		148	1.56	0.56
		144	1.49	0.51
	Average	148	1.54	0.52
	Coefficient of variation	2.6%	2.8%	7.7%
	7	158	1.43	0.52
		142	1.36	0.54
	Average	150	1.39	0.53
	Coefficient of variation			
	28	150	1.45	0.61
		125	1.59	0.48
		138	1.39	0.41
	Average	138	1.48	0.50
	Coefficient of variation	9.3%	7.1%	20.7%
16	1	246	4.64	2.06
		269	5.02	2.21
		234	4.30	1.60
	Average	250	4.66	1.96
	Coefficient of variation	7.1%	7.7%	16.3%
	7	156	2.34	1.00
		166	2.55	1.05
		172	2.38	1.32
	Average	165	2.42	1.12
	Coefficient of variation	5.1%	4.5%	15.4%
	28	136	2.33	1.00
		159	2.15	0.97
		124	2.14	0.92

Table 3 - continued

Mix number	Wet curing time (days)	Initial conductivity (μS/cm)	Chloride conductivity (mS/cm)	2 week chloride conductivity (mS/cm)
	Average	140	2.21	0.96
	Coefficient of variation	12.9%	4.8%	4.2%
17	1	171	0.85	0.51
		172	0.90	0.59
		174	0.89	0.53
	Average	173	0.88	0.54
	Coefficient of variation	0.9%	2.9%	8.0%
	7	131	0.79	0.41
		116	0.68	0.35
		130	0.72	0.38
	Average	126	0.73	0.38
	Coefficient of variation	6.5%	7.9%	8.5%
	28	136	0.81	0.41
		105	0.66	0.34
		110	0.64	0.31
	Average	117	0.70	0.35
	Coefficient of variation	14.3%	13.2%	14.4%
18	1	91	0.91	0.29
		70	0.79	0.27
		72	0.59**	0.25
	Average	78	0.76	0.27
	Coefficient of variation	14.5%	21.3%	7.0%
	7	60	0.49	0.21
		61	0.48	0.21
		46	0.43	0.16
	Average	56	0.46	0.19
	Coefficient of variation	15.7%	6.2%	15.3%
	28	51	0.52	0.22
		53	0.31**	0.22
		47	0.51	0.19
	Average	50	0.44	0.21
	Coefficient of variation	6.2%	26.6%	6.7%
19	1	232	4.68	2.07

Table 3 - continued

Mix number	Wet curing time (days)	Initial conductivity (μS/cm)	Chloride conductivity (mS/cm)	2 week chloride conductivity (mS/cm)
		195	4.61	1.87
	Average	213	4.65	1.97
	Coefficient of variation			
	7	98	1.76	1.37
		74	2.22	1.77
		91	1.77	1.32
	Average	87	1.92	1.49
	Coefficient of variation	14.0%	13.6%	16.7%
	28	48	1.00	0.89
		49	0.81	0.89
		59	0.92	1.00
	Average	52	0.91	0.93
	Coefficient of variation	11.7%	10.4%	6.7%
20	1	208	1.94	0.30
		212	2.73**	0.30
		224	1.82	0.40
	Average	214	2.16	0.34
	Coefficient of variation	3.8%	22.9%	16.7%
	7	98	0.68	0.14
		100	0.84	0.16
		106	0.86	0.18
	Average	101	0.80	0.16
	Coefficient of variation	4.0%	12.2%	10.5%
	28	54	0.60	0.16
		72	0.65	0.16
		60	0.58	0.11
	Average	62	0.61	0.14
	Coefficient of variation	14.4%	6.3%	17.1%
21	1	57	0.23	0.09
		49	0.21	0.10
		52	0.23	0.10
	Average	53	0.22	0.09
	Coefficient of variation	8.1%	4.5%	1.9%
	28	23	0.10	0.06

Table 3 - continued

Mix number	Wet curing time (days)	Initial conductivity (μS/cm)	Chloride conductivity (mS/cm)	2 week chloride conductivity (mS/cm)
		22	0.10	0.08
		19	0.12	0.07
	Average	21	0.11	0.07
	Coefficient of variation	10.1%	7.0%	13.1%
22	1	135	2.75	1.99
		135	3.01	2.09
		131	2.88	1.69
	Average	133	2.88	1.92
	Coefficient of variation	1.7%	4.4%	10.7%
	7	139	2.81	2.00
		140	2.66	1.83
		128	2.80	1.97
	Average	136	2.76	1.93
	Coefficient of variation	5.1%	3.0%	4.9%
	28	122	2.10	2.01
		120	2.24	1.68
		122	2.22	1.67
	Average	121	2.18	1.79
	Coefficient of variation	0.9%	3.3%	10.7%
23	1	140	2.62	1.30
		124	2.61	1.10
		130	2.45	1.04
	Average	131	2.56	1.15
	Coefficient of variation	6.2%	3.7%	11.9%
	7	105	1.52	0.65
		101	1.32	0.60
		108	1.45	0.64
	Average	105	1.43	0.63
	Coefficient of variation	3.4%	7.1%	4.2%
	28	68	0.92	0.44
		69	0.83	0.45
		65	0.80	0.46
	Average	67	0.85	0.45
	Coefficient of variation	3.1%	7.3%	2.2%

Table 3 - continued

Mix number	Wet curing time (days)	Initial conductivity (μS/cm)	Chloride conductivity (mS/cm)	2 week chloride conductivity (mS/cm)
24	1	41	1.13	0.37
		36	-	0.46
		47	1.05	0.34
	Average	41	1.09	0.39
	Coefficient of variation	13.3%	-	16.0%
	7	35	0.47	0.24
		41	0.61	0.25
		37	-	0.31
	Average	38	0.54	0.27
	Coefficient of variation	6.6%	-	11.6%
	28	26	0.19	0.22
		27	0.21	0.17
		25	0.19	0.15
		26	0.20	0.18
		3.1%	4.8%	16.4%
25	1	58	3.23	1.62
		56	3.25	1.60
		59	3.96	1.64
	Average	58	3.48	1.62
	Coefficient of variation	2.6%	11.9%	1.2%
	7	49	1.46	0.62
		54	1.79	0.89
		55	1.57	0.80
	Average	53	1.61	0.77
	Coefficient of variation	6.1%	10.5%	17.9%
	28	34	1.26	0.57
		35	1.12	0.51
		34	1.29	0.58
	Average	34	1.22	0.55
	Coefficient of variation	1.7%	7.4%	6.8%
26	1		1.80	0.29
			1.84	0.26
		Interpolated	1.39	0.25
	Average	67	1.68	0.27

Table 3 - continued

Mix number	Wet curing time (days)	Initial conductivity (μS/cm)	Chloride conductivity (mS/cm)	2 week chloride conductivity (mS/cm)
	Coefficient of variation		14.7%	8.1%
	7		1.04	0.22
			0.69*	0.20
		Interpolated	1.02	0.21
	Average	46	0.92	0.21
	Coefficient of variation		21.3%	5.2%
	28		0.38	0.18
			0.45	0.18
		Interpolated	0.50	0.18
	Average	22	0.44	0.18
	Coefficient of variation		13.2%	0.7%
27	1	62	0.94	0.15
		62	0.94	0.11
		70	1.18	0.15
	Average	64	1.02	0.14
	Coefficient of variation	7.4%	13.8%	19.2%
	7	41	0.40	0.15
		36	0.34	0.12
		39	0.44	0.09
	Average	39	0.40	0.12
	Coefficient of variation	6.6%	12.7%	25.4%
	28	30	0.29	0.08
		34	0.33	0.13
		36	0.33	0.12
	Average	33	0.32	0.11
	Coefficient of variation	10.1%	8.5%	22.5%
28	1	128	2.72	0.39
		118	3.07	0.52
		119	3.25	0.43
	Average	122	3.01	0.45
	Coefficient of variation	4.4%	8.9%	15.3%
	7	72	1.65	0.33
		68	1.27	0.27
		70	1.45	0.34

Table 3 - continued

Mix number	Wet curing time (days)	Initial conductivity (μS/cm)	Chloride conductivity (mS/cm)	2 week chloride conductivity (mS/cm)
	Average	70	1.46	0.31
	Coefficient of variation	3.0%	13.0%	11.1%
	28	40	0.75	0.21
		41	0.85	0.22
		42	0.87	0.23
	Average	41	0.82	0.22
	Coefficient of variation	3.1%	7.8%	4.1%
29	1	53	0.83**	0.14
		62	1.33	0.17
		53	1.30	0.13
	Average	56	1.15	0.15
	Coefficient of variation	9.4%	24.0%	15.3%
	7	28	0.42	0.13
		24	0.37	0.14
		27	0.37	0.14
	Average	27	0.39	0.14
	Coefficient of variation	7.6%	7.4%	2.3%
	28	20	0.37	0.11
			0.35	0.13
		17	0.30	0.13
	Average	19	0.34	0.13
	Coefficient of variation	6.6%	10.7%	8.7%

Table 3 - continued

Mix number	Wet curing time (days)	Initial conductivity (μS/cm)	Chloride conductivity (mS/cm)	2 week chloride conductivity (mS/cm)
30	1	88	1.86	1.60
		108	2.02	1.01
		91	2.28	0.93
	Average	96	2.06	1.18
	Coefficient of variation	11.1%	10.3%	31.0%
	7	93	1.36	1.16
		93	1.36	1.17
		82	1.22	1.07
	Average	90	1.31	1.13
	Coefficient of variation	7.2%	5.9%	5.1%
	28	121	1.50	1.49
		100	1.32	1.56
		106	1.39	1.57
	Average	109	1.40	1.54
	Coefficient of variation	10.0%	6.4%	3.0%
32	1	105	2.94	1.03
		106	2.58	0.93
		92	2.67	0.82
	Average	101	2.73	0.93
	Coefficient of variation	7.6%	6.7%	11.1%
	7	105	2.35	1.28
		99	2.05	1.08
		85	1.95	1.12
	Average	96	2.12	1.16
	Coefficient of variation	10.3%	9.7%	9.3%
	28	118	2.07	1.27
		145	2.43	1.51
		110	2.04	1.27
	Average	125	2.18	1.35
	Coefficient of variation	14.8%	10.1%	10.2%
34	1	Untestable: concrete too weak for coring procedure		
	Average			

Table 3 - continued

Mix number	Wet curing time (days)	Initial conductivity (μS/cm)	Chloride conductivity (mS/cm)	2 week chloride conductivity (mS/cm)
	Coefficient of variation			
	7	34.5	1.77	
		41.8	1.76	
		38.9	1.58	
	Average	38.4	1.70	
	Coefficient of variation	9.55%	6.34%	
	28	16.2	0.74	
		17.1	0.90	
		13.7	0.64	
	Average	15.7	0.76	
	Coefficient of variation	11.2%	17.21%	
35	1	35	1.97	
		37	2.20	
		43	2.40	
	Average	38	2.19	
	Coefficient of variation	10.8%	9.8%	
	7	18	0.27	
		17	0.26	
		22	0.36*	
	Average	19	0.30	
	Coefficient of variation	13.5%	17.9%	
	28	15	0.27	
		15	0.27	
		18	0.28	
	Average	16	0.28	
	Coefficient of variation	10.4%	2.5%	
36	1	71	0.66	
		65	0.51	
		72	0.53	
	Average	69	0.57	
	Coefficient of variation	5.4%	14.4%	
	7	17	0.18	
		21	0.17	
		19	0.19	

Table 3 - continued

Mix number	Wet curing time (days)	Initial conductivity (μS/cm)	Chloride conductivity (mS/cm)	2 week chloride conductivity (mS/cm)
	Average	19	0.18	
	Coefficient of variation	10.3%	4.0%	
	28	24	0.16	
		19	0.17	
		21	0.18	
	Average	21	0.17	
	Coefficient of variation	11.6%	7.3%	

PPC TECHNICAL SERVICES
CEMENT AND CONCRETE LABORATORY

STANDARD REPORT
UCT RESEARCH PROJECT

REFERENCE : T930658 11 NOVEMBER 1993
JOB NUMBER : 84/93

1. **OBJECT :** Refer memo C:\WP51\Docs\MJK\0169.53

2. **SAMPLES :**

Z1211 - Riebeeck West OPC	(UCT Project)
Z1212 - Riebeeck West LASRC	(UCT Project)
Z1284 - Riebeeck West PC30FA	(UCT Project)
Z1285 - Riebeeck West PC50FA	(UCT Project)
Z1288 - Riebeeck West PC50SL	(UCT Project)
Z1286 - De Hoek PC30FA	(UCT Project)
Z1287 - De Hoek PC50FA	(UCT Project)
Z1290 - De Hoek PC50SL	(UCT Project)
Z1291 - De Hoek PC70SL	(UCT Project)
Z1182 - Slurry SRC	(UCT Project)
Z1167 - De Hoek OPC	(UCT Project)

3. **SAMPLE METHOD :**

3.1	SAMPLED BY	:	Refer Riebeeck and De Hoek
3.2	DATE SAMPLED	:	2 August 1993
3.3	SOURCE	:	Refer Riebeeck and De Hoek

4. **TESTS REQUIRED :** Accredited tests.
Density
Specific surface
BS12
Standard Consistency
Setting time
Soundness (Le Chatelier Expansion)
Residues
False set
ISO (Cement mortar prism)
VMC (Cement mortar cubes)

5. **TEST METHODS :**
Refer to Appendix A for accredited test methods.

6. **RESULTS :**
Refer to attached sheet for results.

REFERENCE : T930658 UCT RESEARCH PROJECT 11 NOVEMBER 1993

APPENDIX A
STANDARD LABORATORY REPORT : TEST METHODS

Item	Test	Method
* 1	Relative Density	SABS METHOD 747: Density of Cement
* 2	Specific Surface	SABS METHOD 748: Specific Surface of Cement
* 3	Standard Consistency	SABS METHOD 751: Standard Consistency of Cement
* 4	Setting Times	SABS METHOD 752: Setting times of Cement
* 5	Soundness	SABS METHOD 753 : Soundness of Cement
* 6	Residues	SABS METHOD 746 : Coarse Particle Content of Cement, modified to employ an Alpine Jetsieve and 212 and 90 micron sieves
* 7	False Set	TS/PT METHOD CE10
* 8	ISO	METHOD EN 196 : (PART 1) Methods of testing cement, determination of strength
* 9	VMC	SABS METHOD 749 : Compressive strength of cement mortar cubes
* 10	BS12	BS 4550, PART 3 : SECTION 3.4 : 1978 Physical strength tests

7. The above tests were carried out from 2.8.93 to 14.9.93.

8. The results of the test report are only valid from the samples tested and listed under Item 2 of this report.

G. VAN DER MERWE
C&C LAB SUPERVISOR

J.M. GAYLARD
MANAGER GROUP TECHNICAL SERVICES

6. RESULTS
6.1 Sample Report

SAMPLE NO		Z1211	Z1212	Z1284	Z1285	Z1288	Z1286	Z1287	Z1290	Z1291	Z1182	Z1167
	ACCURACY											
RELATIVE DENSITY	.01	3.14	3.17	2.73	2.57	2.98	2.82	2.61	3.00	2.96	3.20	3.13
SPECIFIC SURFACE	50 cm²/g	2900	3000	3050	2950	3000	3000	3550	3250	3350	4500	2700
STANDARD CONSISTENCY	.1%	25.0	24.0	24.4	24.2	26.2	23.5	24.0	27.0	28.0	25.2	24.0
FALSE SET	1 mm	0	0	0	0	0	0	0	0	0	0	0
INITIAL SETTING TIME	5 min.	190	280	270	325	270	240	310	280	320	260	220
FINAL SETTING TIME	.25 hrs.	4.25	5.50	5.50	6.25	5.25	5.00	6.00	5.50	6.50	5.00	4.75
LE CHATELIER EXPANSION	1 mm	0	1	1	0	0	1	1	1	0	1	*I/S
RESIDUE 90 micron	.1%	3.0	1.4	2.4	2.0	2.2	3.0	3.2	2.6	2.0	0.4	*I/S
RESIDUE 212 micron	.1%	0.0	0.0	0.0	0.0	0.0	0.2	0.0	0.4	0.4	0.0	*I/S
ISO 3 day	.5 MPa	23.5	19.0	13.0	7.5	10.5	14.5	9.0	10.5	5.5	19.5	20.0
ISO 7 day	.5 MPa	31.0	29.0	19.5	12.0	20.5	17.0	12.0	18.5	13.5	28.0	25.5
ISO 28 day	.5 MPa	46.5	47.0	33.5	23.0	41.5	31.0	24.0	37.5	30.0	36.5	40.0
VMC 3 day	.5 MPa	32.5	36.5	21.0	12.5	19.0	21.5	14.0	17.5	10.5	37.5	30.5
VMC 7 day	.5 MPa	45.5	49.5	33.0	20.5	31.5	29.5	21.5	30.5	21.5	45.0	43.0
VMC 28 day	.5 MPa	45.5	60.5	43.0	31.0	47.0	37.5	30.5	52.0	27.0	58.5	50.5
BS12 1 day	.5 MPa	7.5	8.0	4.5	5.0	3.0	4.5	2.5	3.0	1.5	9.0	6.5
BS12 3 day	.5 MPa	16.5	19.5	11.0	7.0	9.0	11.5	7.0	8.5	5.5	19.5	15.5
BS12 7 day	.5 MPa	24.5	25.5	18.0	9.5	16.0	16.0	10.5	14.5	11.5	25.0	22.0
BS12 28 day	.5 MPa	32.5	34.5	27.0	18.5	33.5	23.0	17.0	30.5	27.0	34.5	28.5

Table A2.4: Chloride profiles.

Block number, and depth increments (mm)	Average depth of drillings (mm)	Acid soluble chloride contents			Apparent chloride diffusion coefficient D_a ($\times 10^{-8}$ cm^2/s)
		Chloride content (% w.r.t. conc.)	Chloride content (% w.r.t. cem.)	Fitted curve, (% w.r.t. cem.)	
2 (15)	0			1.53	10.5
	7.5	0.166	1.19	1.18	
	22.5	0.076	0.54	0.58	
	37.5	0.031	0.22	0.22	
	52.5	0.020	0.14	0.06	
	67.5			0.01	
3 (15)	0			1.68	27.6
	7.5	0.197	1.32	1.44	
	22.5	0.180	1.21	0.99	
	37.5	0.090	0.60	0.61	
	52.5	0.032	0.21	0.35	
	67.5			0.18	
4 (15)	0			2.35	4660
	7.5	0.204	2.32	2.32	
	22.5	0.201	2.28	2.27	
	37.5	0.193	2.19	2.22	
	52.5	0.192	2.18	2.16	
	67.5			2.11	
5 (15)	0			1.56	67.6
	7.5	0.179	1.33	1.41	
	22.5	0.165	1.22	1.14	
	37.5	0.132	0.98	0.88	
	52.5	0.070	0.52	0.65	
	67.5			0.46	
6 (15)	0			1.70	33.8
	7.5	0.224	1.43	1.48	
	22.5	0.181	1.15	1.06	
	37.5	0.108	0.69	0.70	
	52.5	0.061	0.39	0.43	
	67.5			0.24	
8 (15)	0			2.10	560
	7.5	0.186	1.98	2.03	
	22.5	0.184	1.96	1.90	
	37.5	0.173	1.84	1.76	
	52.5	0.147	1.56	1.64	
	67.5			1.51	

Table A2.4 - continued

Block number, and depth increments (mm)	Average depth of drillings (mm)	Acid soluble chloride contents			Apparent chloride diffusion coefficient D_a (x 10^{-8} cm^2/s)
		Chloride content (% w.r.t. conc.)	Chloride content (% w.r.t. cem.)	Fitted curve, (% w.r.t. cem.)	
9 (15)	0			1.37	4.5
	7.5	0.158	1.18	1.25	
	22.5	0.156	1.16	1.02	
	37.5	0.105	0.78	0.80	
	52.5	0.076	0.57	0.60	
	67.5			0.44	
10 (15)	0			2.20	42.7
	7.5	0.267	1.96	1.94	
	22.5	0.177	1.30	1.46	
	37.5	0.173	1.27	1.03	
	52.5	0.071	0.52	0.68	
	67.5			0.42	
11 (15)	0			2.18	13.2
	7.5	0.272	1.72	1.73	
	22.5	0.151	0.96	0.94	
	37.5	0.069	0.44	0.42	
	52.5	0.016	0.10	0.15	
	67.5			0.04	
12 (15)	0			3.20	46.5
	7.5	0.272	2.69	2.84	
	22.5	0.253	2.50	2.17	
	37.5	0.157	1.55	1.55	
	52.5	0.089	0.88	1.05	
	67.5			0.68	
13 (15)	0			[illegible]	17.6
	7.5	0.259	1.77	1.72	
	22.5	0.135	0.92	1.04	
	37.5	0.100	0.68	0.54	
	52.5	0.030	0.21	0.24	
	67.5			0.09	
16 (25)	0			3.44	15.3
	12.5	0.250	2.45	2.44	
	37.5	0.089	0.87	0.90	
	62.5	0.026	0.25	0.21	
	87.5	0.008	0.08	0.03	
	112.5			0.00	

Table A2.4 - continued

Block number, and depth increments (mm)	Average depth of drillings (mm)	Acid soluble chloride contents			Apparent chloride diffusion coefficient D_s ($\times 10^{-8}$ cm^2/s)
		Chloride content (% w.r.t. conc.)	Chloride content (% w.r.t. cem.)	Fitted curve, (% w.r.t. cem.)	
17 (15)				3.00	1.05
	7.5	0.183	1.17	1.17	
	22.5	0.007	0.04	0.03	
	37.5	0.000	0.00	0.00	
	52.5	0.000	0.00	0.00	
	67.5			0.00	
18 (10)	0			1.40	1.3
	5	0.160	0.85	0.85	
	15	0.029	0.15	0.18	
	25	0.013	0.07	0.02	
	35	0.000	0.00	0.00	
	45			0.00	
21 (10)	0			1.26	4.4
	5	0.179	0.95	0.98	
	15	0.095	0.50	0.50	
	25	0.017	0.09	0.21	
	35	0.019	0.10	0.07	
	45			0.02	
22 (15)	0			2.31	83.3
	7.5	-	-	2.13	
	22.5	0.220	1.87	1.78	
	37.5	0.186	1.58	1.46	
	52.5	0.107	0.90	1.15	
	67.5			0.89	
23 (15)	0			2.81	2.47
	7.5	0.265	1.63	1.62	
	22.5	0.038	0.24	0.27	
	37.5	0.020	0.12	0.02	
	52.5	0.009	0.06	0.00	
	67.5			0.00	
24 (15)	0			1.34	15.4
	7.5	0.214	1.05	1.10	
	22.5	0.148	0.72	0.67	
	37.5	0.047	0.23	0.35	
	52.5	0.023	0.11	0.16	
	67.5			0.06	

Table A2.4 - continued

Block number, and depth increments (mm)	Average depth of drillings (mm)	Acid soluble chloride contents			Apparent chloride diffusion coefficient D_a ($\times 10^{-8}$ cm^2/s)
		Chloride content (% w.r.t. conc.)	Chloride content (% w.r.t. cem.)	Fitted curve, (% w.r.t. cem.)	
25 (25)	0			4.99	10.8
	12.5	0.29761	3.16	3.15	
	37.5	0.06613	0.70	0.75	
	62.5	0.02311	0.25	0.08	
	87.5	0.01242	0.13	0.00	
	112.5			0.00	
26 (15)	0			2.51	7.17
	7.5	0.2557	1.81	1.82	
	22.5	0.1047	0.74	0.72	
	37.5	0.0231	0.16	0.20	
	52.5	0.0102	0.07	0.04	
	67.5			0.00	
27 (10)	0			1.54	1.34
	5	0.14979	0.90	0.90	
	15	0.02427	0.15	0.16	
	25	0.00782	0.05	0.01	
	35	0.00594	0.04	0.00	
	45			0.00	
35 (15)	0			2.73	2.86
	7.5	0.2331	1.58	1.57	
	22.5	0.03211	0.22	0.26	
	37.5	0.0296	0.20	0.01	
	52.5	0.02107	0.14	0.00	
	67.5			0.00	
36 (10)	0			1.47	1.37
	5	0.1763	0.87	0.87	
	15	0.0285	0.14	0.16	
	25	0.02131	0.10	0.01	
	35	0.02099	0.10	0.00	
	45			0.00	

The mixes not represented in table A10 were either scrapped from the programme (White cement mixes: 30, 31, 32 and 33), disappeared from site (14, 15, 19 and 20), or were not cast due to a lack of cement (7, 28 and 29). Mix 1 is present at the exposure site, but was overlooked and will be tested after 2 years. Mix 34 was cast at a later stage, and placed at the exposure site in August 1996.